# FATE OF CHEMICALS IN SEWAGE TREATMENT FACILITIES

Proceedings of a Seminar held
at the
Radisson Hotel, London

November 23, 1989

sponsored and organized by:

POLLUTION CONTROL ASSOCIATION OF ONTARIO

and the

ONTARIO MINISTRY OF THE ENVIRONMENT

Seminar Co-Chairmen:
Dusanka Filipovic,
Union Carbide Canada Ltd.
Isobel Heathcote,
University of Toronto
Gord Speirs,
Environment Canada

92-01920/

TABLE OF CONTENTS

Page

FATE OF CHEMICALS IN MUNICIPAL SEWAGE TREATMENT FACILITIES: AN OVERVIEW 1
James MacLaren,
Consulting Engineer

LEGAL IMPLICATIONS OF SEWER USE PROGRAM (ABSTRACT ONLY) 39
Metro Patel, Legal Services Branch,
Ontario Ministry of the Environment

CONTROLLING QUALITY IN THE ANALYTICAL LABORATORY 41
Donald King, Laboratory Services Branch
Ontario Ministry of the Environment

VARIABILITY OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WATER POLLUTION CONTROL PLANT INFLUENTS AND EFFLUENTS 49
Stephen Nutt,
CH2M Hill Engineering Ltd.

STRIPPING OF VOLATILE ORGANIC COMPOUNDS AT MUNICIPAL WASTEWATER TREATMENT PLANTS 63
Henryk Melcer, Environment Canada
Wastewater Technology Centre

MUNICIPAL SLUDGE, ORGANIC CONTAMINANTS AND AGRICULTURAL UTILIZATION 83
M.D. Webber, Environment Canada
Wastewater Technology Centre

MODELS FOR PREDICTING THE FATE OF HAZARDOUS CONTAMINANTS IN WASTEWATER TREATMENT PLANTS 99
John Bell,
Enviromega Ltd.

OCCUPATIONAL ASSESSMENT OF EXPOSURE TO CHEMICALS AT METROPOLITAN TORONTO SEWAGE TREATMENT PLANTS 129
Kirby James,
Municipality of Metropolitan Toronto

SURVEY OF ONTARIO MUNICIPAL TREATMENT PLANT EFFLUENT TOXICITY 139
Hugh Monteith, Water Resources Branch
Ontario Ministry of the Environment

ENVIRONMENTAL PATHWAYS OF CONTAMINANTS IN WATERS RECEIVING MUNICIPAL/INDUSTRIAL EFFLUENTS (ABSTRACT ONLY) 147
John Carey, Environment Canada
National Water Research Institute

# FATE OF CHEMICALS IN MUNICIPAL SEWAGE TREATMENT FACILITIES AN OVERVIEW

---

*J.W. MacLaren, p.eng.*

*October 1989*

*A paper to be presented before*
*A joint PCAO/MOE Seminar in London, Ontario*
*November 23, 1989*

# FATE OF CHEMICALS IN MUNICIPAL SEWAGE TREATMENT FACILITIES - AN OVERVIEW

## INDEX

**ABSTRACT**

**KEYWORDS**

**TABLES**

**CONTENTS**

1. Introduction
2. U.S.-Canada Great Lakes Water Quality Agreement
3. MISA Program - General
4. MISA Program - Municipal
5. Effectiveness of Exiting MSTPs in Toxic Removal
6. Municipal Pollution and Toxic Abatement Programs for Waste Water in the United States
7. Findings and Cost Estimates

**REFERENCES**

# TABLES

I. 37 Plant Monitoring Study - Toxic Presence & Reduction Approximations [5]

II. Removal of Volatile Organic Compounds [6]

III. Comparison of Organic Pollutant Removals by two Activated Sludge Plants [6]

IV. Average concentrations [ug/L] of VOCs in influent and effluent at the Calumet and West-South West Plants [7]

V. Best estimates of VOC removals by all three mechanisms at the Calumet WPCP [7]

VI. YARDSTICKS - 27 Pollutants to be regulated over 5 Disposal Options [17]

VII. Non-Agricultural Land Pollutant Limits [18]

VIII. Current Average Annual Household Costs for Environmental Services [1988] [21]

IX. Current and Potential Additional Average Annual Household Costs for Improved Environmental Services [1988] [21]

# FATE OF CHEMICALS IN MUNICIPAL SEWAGE TREATMENT FACILITIES - AN OVERVIEW

**James W. MacLaren, p.eng**

ABSTRACT - Current arrangements between Canada and the United States of America require the virtual elimination of toxic substances from the Great Lakes by 1995. Ontario is committed to this objective under the ***"MUNICIPAL AND INDUSTRIAL STRATEGY FOR ABATEMENT".*** In that program the 399 municipal sewage treatment plants will be required to be upgraded so as to virtually eliminate chemical pollutants from their discharges, according to municipal effluent regulations scheduled to be enforced by the end of 1992. Chemicals reaching municipal sewage systems will be required to be reduced through source reduction or process change by approximately 11,000 industries discharging to these systems, while residual concentrations reaching these plants must be removed to meet toxicity requirements without threat to air or sludge streams nor to the operating atmosphere within these plants.

Is this a fair challenge and realistic objective? Can it be achieved in the light of current experience, especially based on the progress of the United States Environmental Protection Administration with publicly-operated treatment works?

This paper attempts to address these crucial issues in determining the fate of chemical and hazardous materials within municipal sewerage systems and treatment works.

KEY WORDS - *TOXIC, MUNICIPAL, FATE, CHEMICAL, TREATMENT*

## *1.* ***INTRODUCTION***

It is essential when considering the issue of hazardous and toxic materials, the need for their elimination from the aquatic ecosystem and their subsequent environmentally-sound disposal to understand the threat that these chemicals pose to humans and to the life and land around us.

A colleague of mine on the MISA Advisory Committee, **Dr. Donald Mackay** of the University of Toronto put the issue in sound layman terms when speaking to the Ontario Section of the American Water Works Association in London, Ontario in May 1988 (1). He pointed out that currently the Ontario Ministry of the Environment [MOE] lists 234 chemicals as Effluent Monitoring Priority Pollutants [EMPPL] which may be present in Ontario waters and are regarded as sufficiently toxic to be of concern and so are candidates for control [and the list continues to grow].

Dr. Mackay suggests that there are three properties [the three D's as he calls them] of these chemicals that are cause for real concern and why we are faced with their control.

First are chemicals which are ***DISTRIBUTIVE*** or which bio-concentrate so one nanogram of PCB in a litre of water or one ppb could concentrate in fish to one ppm permitting one mouthful of fish to equal one million mouthfuls of water in human exposure.

Second are chemicals that could be termed ***"DIRECTIVE"*** or which influence the growth patterns of organisms. Chemicals which in tiny amounts are able to affect the organism by directing its growth patterns along undesirable pathways causing carcinogenetic or mutagenetic conditions. Thalidomide was a tragic example.

Finally ***DURABILITY*** or persistence of chemicals to last for a distinct lifetime in the environment permits long term exposure of organisms and humans to their impact. Radon gas within the home is a very real example.

All chemicals, therefore, of a polluting or a toxic nature have the potential of pervading air, water, soil and sediment and whether in synergistic or antagonistic posture have in concert the opportunity of destroying our ecosystems. Where conventional pollutants and nutrient excesses have been our immediate concern and still must be of a high priority, toxic materials in our environment have become life threatening.

## 2. *U.S. - CANADA GREAT LAKES WATER QUALITY AGREEMENT*

Little wonder, therefore, that the Governments of Canada and the United States in their Agreement of 1978 on Great Lakes Water Quality in ***"reaffirming their determination to restore and enhance water quality in the Great Lakes System"*** agreed to ***"make a maximum effort to develop programs, practices and technology necessary for a better understanding of the Great Lakes Basin Ecosystem and to eliminate or reduce to the maximum extent practicable the discharge of pollutants into the Great Lakes System".***

Consistent with the provisions of that objective, it is the policy of both Parties that:

a) "The discharge of toxic substances in toxic amounts be prohibited and the discharge of any or all persistent toxic substances be virtually eliminated;

b) Financial assistance to construct publicly-owned waste treatment works be provided by a combination of local, state, provincial and federal participation; and

c) Coordinated planning processes and best management practices be developed and implemented by the respective jurisdictions to ensure adequate control of all sources of pollutants."

Subsequent amendments to this Agreement dated October 1983 and November 1987 have simply served to strengthen the resolve of the Parties in their original commitment especially with respect to persistent toxic substances. Amendments indicate the need for improved management procedures to achieve the objectives in view of the fact that persistent toxics enter waters not only from direct discharges, but from the air, from ground water infiltration, from sediments in the lakes and from runoff at non-point sources.

To that end the parties recognized based on data provided by the International Joint Commission* through its Advisory Boards that there are certain areas of the Lakes where the objectives are not being met. They agreed to eliminate these areas of concern including their critical pollutants and their point source impacts through Remedial Action Plans, on a priority basis as well as developing Lakewide Management Plans to address toxic pollutants.

Indeed all aspects of the agreement are directed to restoring the aquatic ecosystem and improving water quality throughout the Great Lakes System by the adoption of these common objectives, developing and implementing cooperative programs and other measures.

Of special interest to municipalities is the requirement with the co-operation of State and Provincial Governments that the general and specific objectives will be met by instituting "programs for the abatement control and prevention of municipal point discharges and urban runoff discharges into the Great Lakes System." These programs shall be completed and in operation as soon as practical and shall include:

i) Construction and operation of waste treatment facilities in all municipalities having sewer systems to provide levels of treatment consistent with the achievement of phosphorus removal requirements and the General and Specific Objectives, taking into account the effect of wastes from other sources (MISA);

ii) Provision for financial resources to assure prompt construction of needed facilities (MISA);

iii) Establishment of construction and operating standards for facilities;

iv) Establishment of pre-treatment for all industrial plants discharging waste into publicly-owned treatment works where such industrial wastes are not amendable to adequate treatment or removal using conventional municipal treatment processes [MISA];

v) Development and implementation of practical programs for reducing pollution from storm, sanitary and combined sewers; and

vi) Establishment of effective enforced programs to ensure that the above pollution abatement requirements are fully met.

Of import to the foregoing are the Specific Objectives. Here the agreement sets out a list of 260 substances believed to be present in the Great Lakes and known to have toxic effects on aquatic and animal life and as well as a list of 105 additional substances also believed to be present and potentially having such effects including risk of discharge with a requirement of giving priority to the examination of these latter substances for transfer to the first list. Programs and measures will be developed to minimize or eliminate the risk of release of these hazardous polluting substances.

---

* The Commission has been given the responsibility under the Boundary Waters Act of 1911 of managing all water quality data and tendering advice and recommendations to the Parties on problems and matters relating to the quality of the Boundary Waters and achievement of the Agreements's objectives.

The criteria that are applied to the selection of substances as candidates for testing as toxic substances are their acute toxicological effects as determined by lethality tests such as one half of a test population of aquatic animals being killed in 96 hours or less at a concentration of 500 milligrams per litre ($LC_{50}$).

## *3. MISA PROGRAM - GENERAL*

With the foregoing agreement and its amendments in place, both federal governments are to require their respective states and provinces to comply with these commitments. U.S. states are not committed by a Federal agreement so that the United States is forced to use its powers under the U.S. Clean Water Act and its amendments to require enforcement. If a state has elected to cooperate in the National Pollutant Discharge Elimination System **(NPDES)** of the Clean Water Act, these federal requirements are enforced through the state; if not they are directly enforced. The weakness of course is that the U.S. can only enforce under the Agreement the conditions of the Clean Water Act. If they are more or less stringent than the requirements of the agreement, so be it. Ontario, however, is bound by Canada's international commitments under the Constitution Act. This is confirmed by a Canada Ontario Water Quality Accord or the province's direct witnessing of the agreement and its amendments.

As a result and in confirmation of its responsibilities, the Honourable Jim E. Bradley, Minister of Environment in Ontario introduced the **Municipal Industrial Strategy for Abatement (MISA)** for controlling Municipal and Industrial Discharges into all Ontario surface waters, not just the Great Lakes in June of 1986.

This program literally responded to the requirements of the Great Lakes Water Quality Agreement. It sets effluent limits to point discharges from each major industrial sector directly discharging to waterways as well as the municipal sector on the basis of two complimentary approaches.

1. **BAT Approach** - the Ministry will develop regulations setting effluent limits for major industrial sectors and the municipal sector. Effluent limits initially will be based on the use of the best available technology that is economically achievable for each sector. Here the statutory assessment of **BAT** considers costs, but does not require a balancing of costs against effluent reduction benefits. The primary determination of **BAT** is effluent reduction capability. In addition to a number of treatment-before-discharge technologies, **BAT** may include process changes in the plant, substitution of chemicals, improved treatment technologies, recycling and reduced water usage.

2. **Water Quality Impact Approach** - Dischargers will be required to carry out receiving water assessments to evaluate the water quality impacts of the various toxic contaminant levels in their effluents. After evaluation of these assessments, site-specific effluent limits will be set to best protect water quality.

For a given site, the requirements of the two approaches will be compared and the discharger will be required to comply with the more stringent of the two limits.

The **BAT** technology may not be employed at the expense of increasing toxics discharged to the air (reg.308) or to sludges (reg.309). These regulations will be strengthened so as to reflect an integrated ecosystem approach to toxic elimination.

## 3. *MISA PROGRAM - MUNICIPAL*

The Ontario Ministry of the Environment has further outlined its approach under the **MISA** program to municipal point discharges with the issuance in September 1988 of the ***White Paper*** entitled *"Controlling Industrial Discharges to Municipal Sewers".*

Based on directives issued to the time of preparing this paper, the Municipal program to control toxics in waste water and thereby determine their fate appears as follows:

**A.** Sewer Use Program Regulation to be issued by MOE (Yet to be Released)

- Setting out the objectives of eliminating toxic and hazardous materials at the source;
- Cataloguing all direct discharges to Municipal sewers in excess of household volumes - setting **BATEA** industrial categories as well defining significant dischargers as discharging 114 cu. meters per day, or more than five percent of flow or flow strength, industry annual reports, **IDIMIS** audits;
- Setting control requirements - **BATEA** effluent limits for 22 industrial categories, local limits, prohibited substances, spills management, industrial discharge management plans;
- Enforcement
  - municipal enforcement and MOE audits
  - industrial self-monitoring
  - user charges and permitting system.
- Scheduling

**N.B.** The municipal sector refers to municipal sewage treatment plants **(MSTPs)** and their related systems of sewers. American regulations frequently refer to **MSTPs** as publicly-owned treatment works **(POTW's)** or **Water Pollution Control Plants (WPCPs).**

B. **Municipal Enforcement Program** (To follow Sewer Use Regulations)

- Municipalities involved (only 90 initially, 4500 c.m. per day or more with the remaining 309 to follow);
- Development and enforcement plan
- Proof of ability to develop plan
  - enforcement mechanism to implement the plan
  - permit system to authorize sewer access
  - enforcement action proposed
  - staffing and resources to be provided
- Industry inventory and its management system
- Municipal sewer use by-law and permit system
  - industrial limits
  - prohibited discharges
  - local limits
- Implementation
  - inspection, sampling, flow measurement for inventory and on-going monitoring of industrial discharges.
  - industrial self-monitoring procedure.
  - data processing and compliance screening.
- Public involvement

C. **Municipal STP/Effluent Limits Regulation** (Yet to be Drafted)

This will be the ultimate document that will set the effluent limits based on secondary treatment to which all plants must conform at a minimum. A ***Water Quality Impact Regulation*** may be required to set out the manner of establishing special requirements in areas where water quality in the receiving waters may dictate tougher effluent standards and the regulation will probably specify a site specific toxic chemical monitoring program including whole effluent toxicity testing.

## *5. EFFECTIVENESS OF EXISTING MSTP'S IN TOXIC REMOVAL*

Typical secondary type **MSTP's** in Ontario have been designed, built and operated primarily for the removal of conventional pollutants such as total suspended solids and 5-day biochemical oxygen demand. Effluent discharge requirements for these plants set by MOE are currently equal but not greater than 25 mg/L for both parameters on an annual average.

All plants discharging effluent to the Great Lakes Watershed must also control total phosphorous in their effluent for eutrophication prevention. This nutrient requirement is currently set by MOE as not exceeding 1.0 mg/L on a monthly average basis and requires chemical additions to the normal plant process thereby creating a form of advanced waste water treatment.

Further nutrient control in the conversion or removal of nitrogen in its various forms is required in specific instances but no provincial standard exists. Nitrogen control will be of increasing importance in Great Lakes waters as evidenced by the recent concerns expressed in the report of the Great Lakes Water Quality Board.

The removal of toxic materials represents a challenge to a secondary treatment system for which it was never designed. The continuous variability of an **MSTP** influent, the impacts of synergism and antagonism, the sensitivity of biological sludges to toxic pollutants and even the quality of the municipal raw water supply make it difficult for present secondary plants to consistently reduce toxic pollutants without some form of pretreatment. In any case toxics that are removed can provide an intolerable problem in sludge treatment and disposal.

Since possible advanced waste water treatment requirements and the treatment of further contaminated sludges can be not only expensive but sometimes difficult to accomplish, it is little wonder that municipalities must consider the control of toxic discharges to their sewerage systems so as to reduce the problem at its source.

Despite the success of such a program, there will still be residual toxics pollutants in the raw sewage flow from residential and uncontrolled sources. The need, therefore, to assess the effectiveness of traditional secondary treatment systems in the removal of a complete mix of hazardous and toxic materials including metals, pesticides, herbicides and PCBs, volatile compounds, base neutral and extractable compounds, dioxins and furans is still important.

The optimizing of source reduction with improved treatment for toxic removal so as to avoid the pass-through of these pollutants or toxic upsets to traditional treatment systems is a complex issue.

To assist its solution, the Ministry of the Environment, Environment Canada and the Ontario Municipal Engineers Association commissioned a consulting engineering firm (CANVIRO), three commercial laboratories plus the MOE Laboratory Services Branch to determine the nature and incidence of toxic and persistent pollutants in MSTP effluents and sludges in 37 representative MSTPs in Ontario (5). (Currently there are 399 publicly-owned treatment works in Ontario of which 232 are owned and/or operated by MOE).

The sample group contained:

- all plants discharging more than 45000 cubic meters of effluent daily and included sixteen secondary plants and seven primary treatment plants;
- an additional five MSTPs monitored in the Upper Great Lakes Connecting Channels program;
- seven geographically spaced MSTPs of a secondary type treating less than 20,000 cubic meters daily;
- two lagoon style facilities.

The results of this work undertaken in 1987 and published in two volumes in December 1986 had not been officially interpreted at the time of writing this paper in early September, 1989.

However certain observations can be made at this time about the general findings on the fate of toxics in these plants. Since MOE's current Effluent Monitoring Priority Pollutants List (EMPPL) of some 234 compounds (144 with protocols) was not available at time of initiating this study, only 144 organic compounds, 15 metals and 14 conventional pollutants representing the original **USEPA Priority Pollutant List** were included in the study.

Of primary concern were the metals because of their durability in the environment. Sampling programs were conducted in winter and summer periods during 1987. Five consecutive days of sampling were carried out in each period. Twenty-five(25) plants were sampled in the winter period and twenty-nine(29) in the summer but seventeen(17) were sampled in both periods. Raw sewage, final effluent, raw sludge and treated sludge were measured, sampled and analyzed.

Coincidence of measuring and sampling for a short period was difficult to assure as were typical conditions for a short flow period. QA/QC results in some instances suggested weaknesses in the recorded data. Plants sampled represented 75 percent of the recorded average daily municipal sewage flow in Ontario area and larger plants evidenced the greatest number of toxics present at the highest frequency of occurrence.

It is only possible to generalize on the results, since to do otherwise would be unfair to the level of effort. **Table I** summarizes random approximations of the results but the following observations might be made.

## RAW SEWAGE

- 85 of the 144 organic contaminants (59%) sampled were present at least once; 14 of the 15 metals (93%) plus cyanide were also present at least once - beryllium being absent.
- strontium, copper, zinc, mercury, aluminum, chromium were present 75% of the time at twenty or more plants, the remainder were present less than 30 percent of the time.
- mean concentrations in micrograms per litre were less than 100 except for strontium, copper, and aluminum.
- geometric mean concentrations for all other toxics were under 25 mg/L with only M-Cresol, Phenol, Butylbenzylphthalate, 2,4-Dichlorophenoxyacetic acid, Gamma-BHC(Hexachlororcyclhexane) (Lindane), Methoxychlor, PCB, 1,2,4-Trichlorobenzene, Silvex and 2,4,5-Trichlorophenoxyacetic acid being present in more than 10 of the plants sampled.

## SECONDARY EFFLUENT

- 68 organic compounds, 14 metals and cyanide were detected at least once in secondary effluent.
- with the exception of strontium which was relatively undiminished all metals were reduced from 65 to 88 percent and appeared less frequently than in raw sewage.
- organics were all reduced substantially in concentration (65 to 100%) and as expected volatiles that remained were encountered in only a few samples at less than five plants and in trace amounts.

## RAW AND TREATED SLUDGE

- 59 of the 144 organic contaminants (41%) sampled were present at least once; all of the metals and cyanide were present at least once, both in a larger number of plants.
- the percentage frequency of detection as well as the frequency of appearance at plants sampled increased substantially due to the concentrating effect of the sludge.
- about the same figures applied to treated sludge with concentration and frequencies increased.
- several contaminants like cyanide had apparently vanished during treatment.

The foregoing demonstrates reasonably well that a large number of priority pollutants were present in municipal sewage and that secondary treatment substantially, drove off the volatiles and significantly reduced the remainder (65 to 90%) concentrating them in the sludge. However, some residual effluent concentrations were still of concern.

Metals were predominant in maintaining their presence at levels higher than considered acceptable in more than 5 instances.

Here in Canada, Monteith's work published as "Fluctuations of Trace Contaminants in Sewage Treatment Plants" by the Waste Water Technology Centre of Environment Canada in 1987 and "Investigations of Stripping of Volatile Compounds in Municipal Waste Water Systems" published by the Ontario Ministry of the Environment in December 1988 confirms these results. He found that in raw municipal wastewater samples, metals, purgeable organics and phthalate esters were the most frequently occurring compounds while in treated effluents metals predominated. He also confirmed that a high percentage of VOCs entering a MSTP are removed in the treatment process.

In support of the foregoing, the **USEPA** in a long term program has been conducting research to determine the ability of waste water processes to remove toxic organics. Spiked samples of 21 priority pollutants were fed to controlled condition pilot activated sludge systems. Removals of volatile organic compounds including those set out in **Table II** averaged 91 present while the removal of other organic pollutants although significant as indicated in **Table III** were more variable showing the difficulty of basing policies and regulations on a heterogenous collection of removability data assembled from different treatment plant surveys and research studies. **Table III** shows deviations from the arithmetic mean in real numbers and indicates that both lindane and pentachlorophenol removals were less than 65 percent (6).

Actually as an example of the difficulty of assuring the reliable removal of an organic contaminant like pentachlorophenol (PCP), studies were undertaken at bench scale by the Waste Water Research Centre of Environment Canada. Removals were found to be extremely sensitive to solids retention time under air. Reductions of 95 percent or better, even with high and shock loadings were possible with 15 days solids retention but in reduced retention times, PCP removals were incomplete resulting in efficiencies of less than 50 percent. The 37-plant study showed a possible reduction for PCP of 78 percent.

The fate of volatile organic contaminants of which there are more than 50 on the current **EMPPL** list is important. Emitted **VOCs** can create potential health hazards for **MSTP** workers and the general public that live adjacent to **MSTPs**. Therefore the assessment of their levels of emission to atmosphere during treatment and the best manner of coping with that condition constitutes a significant element of plant design and operation.

Plant scale studies of the volatile conditions occurring at the Calumet and West-South West **STPs** of the Metropolitan Sanitary District of Great Chicago have done much to clarify our knowledge of the fate of **VOCs**(7). **Table IV** shows the actual removals over 12 months of eleven volatile compounds reaching these plants. Removal efficiencies exceeded 80 percent except in two instances at Calumet. Chloroform and Methylene chloride actually showed gains through treatment, possibly explained by their formations as intermediates or actual products during biodegradation of other compounds.

Researchers at Chicago undertook to determine how much of the **VOC** reductions occurred through biodegradation and adsorption mechanisms rather than volatilization. Using mathematical modelling, they demonstrated as shown in **Table V** that for the Calumet plant biodegradation was primarily responsible for **VOC** removal (71%) (The figure for West-South West plant was lower at 56%). Others have argued that although these total removals are valid, volatilization plays the more substantial role since considerable loss takes place in primary treatment prior to aeration.

In actual fact the literature is loaded with modelling, bench scale testing and full plant experimentation and/or experience with toxics removal in municipal sewage treatment plants. Lester edited a two-volume series which addresses the source, behaviour, fate and environmental significance of heavy metals during conventional waste water treatment and sludge treatment (8). Generally it was found that metal reduction was highest in plants receiving the most toxic effluents which is somewhat substantiated by the 37-plant study. Since **MSTPs** in Ontario are or will be usually of the activated sludge type with primary treatment, it is reasonable to conclude that relatively high removals of the priority pollutants can be achieved where the solids retention time such as in a nitrification mode is maintained in excess of six days. Smaller plants with a narrower but more concentrated range of toxics in the influent will have to be designed for protection from shock loading through pretreatment and/or the provision of powdered activated carbon (PAC). Studies have indicated that the addition of **PAC** to the activated sludge process can significantly improve toxic removals (9).

Certainly the Chicago experience shows that a large activated sludge plant operating at 95 percent conventional pollutant removal efficiency or better with a sludge retention time of six days and mixed liquor solids of at least 2500 g/cubic meter is well buffered to destroy and/or remove most toxics at a level of 90 percent or better (7). Indeed **EPA** estimated in 1986 that in **MSTPs** with biological treatment systems fully acclimated to toxic substances, 92 percent of these contaminants will be removed from effluent discharges (10).

However the more efficient the waste water treatment plant in toxics removal, the greater the concentration of all but the volatiles in the sewage sludge. Canadian studies have shown that sludge handling costs were 47 percent of total annual plant costs (52 percent operating and 46 percent capital) (11). Concentration of pollutants in sludge at a **MSTP** therefore represents considerable additional operating expense. Also the presence of toxics in raw sludge especially metals can have inhibiting effects on standard and high rate anaerobic digestion, sludge conditioning and create emissions and ash problems in incineration as well as increasing the problems of disposal of the treated sludge.

If municipalities, specifically **MSTPs**, are being considered as the treater of last resort - then the disposal of sewage sludge infected with residual toxics will require the consideration of the public and all levels of government to determine a solution which we can all accept as the guilty parties.

## *6. MUNICIPAL POLLUTION AND TOXICS ABATEMENT PROGRAMS FOR WASTE WATER IN THE UNITED STATES*

A reasonable understanding of the United States Regulatory Program with respect to Publicly-Owned Treatment Works (POTWs) and the controls relating to tributary toxic contaminants have considerable significance for Canadians. Since the American program is well advanced, since the Ministry of the Environment has officially adopted the U.S. municipal sewer use control policy as the most suitable option for consideration in Ontario (4) and since Ontario must achieve equal effluent control to the Great Lakes States, the American experience can be invaluable.

The current U.S. municipal waste water treatment program is directed by the **U.S. Environmental Protection Agency** under the terms of the **Federal Water Pollution Control Act** of **1971 [PL92-500]**, the **Clean Water Act [PL95-217], The Municipal Wastewater Treatment Construction Grant Amendments** of **1981 [PL97-117]** and the **Water Quality Act** of **1987 [PL100-4].**

Wastewater treatment plants are built to meet Federal treatment standards, to protect the public health and the environment and to provide for local growth. States determine the order in which federal grants are used to finance local facilities based on local water quality problems; population; per capita income; and local readiness to build. Local governments are responsible for the design, timing, cost-effectiveness and final selection of facilities. But the states ensure local compliance with state water quality plans and minimum design and construction standards. **EPA** sets national policy affecting the type of technology that will qualify for grants and the processes that constitute effective planning.

The flagship in this chronology was the **Water Pollution Control Act** of **1971** which replaced in-stream water quality standards for national limits on the discharge of pollution from **POTWs** and industrial point source discharges. The law had a goal of restoring all navigable waters to "fishable and swimmable" conditions by 1983 and mandated all **POTWs** to provide secondary treatment by 1983, later adjusted to 1988. The federal share under the **Construction Grants program** of capital spending on **POTWs** was set at 75 percent but specified strict procedures to determine the size and extent of facilities to be built. This law established the **National Pollutant Discharge Elimination System [NPDES]** permit system and the authority for the federal government to approve every point source wastewater discharge in the nation. The intent was to delegate this system to the states for operation but only 35 states accepted from **EPA** the obligation and cost of acting to ensure that **NPDES** permitting system was met by municipalities. The remaining states refused in view of management costs, so some 1500 U.S. municipalities had to deal directly with **EPA** under the **NPDES** program.

The **Clean Water Act** of **1977** provided increased funding and encouraged innovative and alternate technologies by offering to pay an extra 10 percent [or a total of 85 percent of capital costs) where these technologies were employed.

But the **Construction Grant Program** of 1981 reduced the federal share as a Reagan policy from 75 to 55 percent for conventional technologies beginning in 1985 and limiting assistance to the needs of current populations only. Treatment standards were expanded to include lagoons, trickling filters etc. and spending was limited to $2.4 billion annually.

Finally in 1987, the **Water Quality Act** authorized a final $18 billion for the construction of wastewater facilities on the basis that the **Grants Program** would be funded at $9.6 billion in 1988 reducing to zero in 1990. Federal grants were to be replaced with **State Revolving Loan Funds** that would receive capitalization grants from **EPA** totalling $8.6 billion from 1989 to 1994. In addition the states were to contribute a minimum of 20 percent of the federal contribution to the **SRF[10]**.

The **Act** also stressed the need, now that the **NPDES** program was in place and secondary treatment established at most **POTWs**, to return to a water quality based approach using a floor of technology-based requirements. The water quality approach could therefore be used to go beyond the technologically based minimum when necessary for a particular receiving water which represents **MOE's** proposed **Water Quality Impact Approach.**

The **Act** also provided for the introduction of the **Whole Effluent Toxicity [WET] program** for **POTW** effluents. **EPA** recognized in this that it was clear that if the **NPDES** program where going to depend on a chemical by chemical control approach, the process would be never ending. (12)

In reference to the foregoing, **EPA** bi-annually assesses the municipal needs of the **Clean Water Program.** In its 1986 review [13], it stated that after the spending of $57 billion in federal grant funds that annual continuing needs to build facilities used in the conveyance, storage, treatment, recycling and reclamation of municipal waste water in 1986 U.S. dollars were:

| | | |
|---|---|---|
| **Category I** | Secondary Treatment - 85% removal by all **POTW's** | $23.9 billion |
| **Category II** | Advanced Waste Water Treatment - 85% of conventional as well as nutrients and toxics | $4.3 billion |
| **Category IIIa** | Infiltration/Inflow - preventing ground water seepage and extraneous flows | $3.0 billion |
| **Category IIIb*** | Replacement/Rehabilitation of deteriorating sewers | $3.0 billion |
| **Category IVa*** | New Collector Sewers to accommodate growth | $12.8 billion |
| **Category IVb** | New Intercepting Sewers - for increased pollution control | $14.4 billion |
| **Category V** | Combined Sewer Overflows - Containment of overflows and **POTW** relief from excess flows | $15.2 billion |
| | **Total:** | **76.6 billion** |

The actual sums are relatively unimportant to Canadians but comparisons of the various components are interesting. Of the total of $76.6 billion in which **Categories IIIb** and **IVa** represent provision for system aging and increased capacity, $60.8 billion or $300 per capita annually must be spent on pollution control (40% for secondary treatment, 7 percent for advanced waste water treatment, 4 percent for 1/1 prevention, 24 percent for new intercepting sewers and 25 percent for combined sewer overflow containment). These represent capital dollars and give some indication of per capita spending requirements in Ontario. It should be noted that the foregoing do not provide for spending relating to control of pollution from storm sewers nor for operating costs.

Returning to the toxics issue the **National Pollution Discharge Elimination System [NPDES]** required municipalities to provide a minimum level of effluent quality through secondary treatment as follows:

1) 30 day average **BOD[5 day]** should not exceed 30 mg/L;
2) 7-day average **BOD[5 day]** shall not exceed 45 mg/L;
3) 30 day average percent removal of **BOD** shall not be less than 85 percent.

Identical figures also apply to suspended solids while pH must be maintained between 6.0 to 9.0. Special consideration is given where combined sewer flows during wet weather dilute the sewage. No industrial discharges may decrease the **POTW** effluent quality to less than would be required of that industrial effluent if it were being discharged directly to a receiving body [14].

With the introduction of the **Water Quality Act** of **1987**, permits are now required to be written in terms of local water quality standards so that the foregoing conventional requirements can be modified to require lower figures (Chicago main plants must reduce pollutants to 95 percent with 30 day averages not exceeding 10 mg/L as well as limits on nutrients and specific toxics). Specific toxic control is governed by **EPA's 1984** directive on permit limitations for toxic materials [15]. **EPA** demands that the first line of defense for municipalities in the control of toxics discharged by industry to municipal sewer system be in the enforcement of the national pretreatment standards (15). These standards are now incorporated into local municipal programs and enforced as part of the municipal **NPDES** permits for **POTWs** having flows in excess of five million United States gallons daily. They are designed to limit industrial discharges from some 22 categories of industries to municipal sewers so that toxic and hazardous pollutants from these sources will not pass through **POTWs** or be incompatible with sewage or sludge treatment. Also by toxic control at the source, recycle and reclamation of industrial waste waters and sludges will be encouraged. The standards as written are similar to Ontario draft sewer use regulations that will be embodied in **Municipal Sewer Use By Law.**

As a result of the foregoing, specific toxic effluent standards are usually only included in **POTW NPDES** permits where there is concern over the prevalence of a specific compound in the particular system. **EPA** is leaning also towards its whole effluent testing program (12). This program is still very controversial over the correct toxicity tests and the appropriate test organisms but it is being written into **POTW** permits. Where consistent failure of toxicity tests occurs then increased enforcement of pre-treatment standards is obvious.

Complimentary to the **NPDES** permit system to control conventional and toxic contaminants in waste water effluents is the need to deal with the residual toxics that do reach the **MSTP** and are removed and concentrated in the primary and secondary sludges. Even with sound system pre-treatment standards in place, **EPA** estimated (17) that:

> *"Metal and organic loadings from domestic sources account for 7.5 and 19.4% respectively of loadings to **POTWs**. This analysis demonstrates that residential sources are small but significant sources of hazardous constituent loadings to **POTWs**".*

Later studies showed that in **POTWs** serving smaller municipalities the impact of toxics in sludges from residential sources was severe.

**EPA** is currently attempting to establish by July 1990 revised draft numerical limits for identified sludge pollutants *"adequate to protect the public health and environment from any reasonably adverse effects"*. The attached **Table VI** lists the 27 sludge contaminants to be regulated over five disposal options (18) while **Table 7** sets out as an example their maximum sewage sludge concentration for non-agricultural lands. Final regulations are due to be promulgated by October 1991. [19]

Risk-based regulations for five different types of sludge disposal: incineration, non-agricultural land application, agricultural land application, distribution/marketing and monofills/surface impoundments have been developed.

Pathway risk analyses from contaminants to humans have been undertaken to set concentrations to less than a 1 to 10,000 chance that metals will be picked up by plants and eaten by humans. Effluent limits for incineration with respect to air emissions, ambient air, incinerator bottom ash and flyash will be set sufficiently to low to reduce risk and will considerably increase current incineration costs.

Containing volatile organic and noxious odours escaping from treatment plant waste water surfaces and enclosed areas is a further issue of concern. Conditions for operating personnel exposed to ambient air in enclosed areas are covered under occupational health and safety standards issued by the U.S. Department of Labour in co-operation with EPA.

Release of volatile organics at the plant site may require all surfaces in major plants to be covered and where appropriate the gases collected and detoxified.

A program as complex as the U.S. program is obviously not without its problems and faults and the following are worthy of note in developing the Ontario program especially in relation to the fate of toxic contaminants:

- Federal funding was so generous that now it has been withdrawn, states and municipalities are staggered by the program remaining and their abilities to finance it;
- Federal generosity covered up hidden operating costs attached to the new facilities but more than that permitted municipalities to continue to set rates for wastewater control services well below their real cost despite EPA regulations designed to prevent this;
- the program which was to take ten years will take at least twenty;
- As of last July, there were still 408 out of 3,722 major and 1,600 minor POTWs in non-compliance with plant treatment standards requiring court-ordered schedules, administrative or direct court action to force compliance; [20]
- when a municipality and EPA cannot come to terms over appropriate corrective compliance action, EPA can and does resort to the Federal Courts which can result in bitter confrontations and substantial penalties;
- now treatment compliance is substantially established at the minimum level of secondary treatment EPA and the states are concentrating on permit enforcement and the implementation of local pre-treatment programs. Industrial interference with POTW operation including pass through is now an area of permit violation which EPA will not tolerate;
- another major area of concern to POTW managers is the tightening of water quality based discharge limits particularly with regard to the introduction of whole effluent toxicity requirements and effluent biomonitoring;
- permit enforcement based on consistent plant performance to effluent parameters is now becoming much more rigid. EPA will not accept the concept of due diligence and the partnership solution to difficult treatment

issues - **POTWs** must perform.

Unfortunately the federal government's own actions and policies may have increased the complexity of the problems many U.S. municipalities face relative to toxics. The passage of the **Hazardous** and **Solid Waste Amendments** to **U.S. Resource Conservation** and **Recovery Act (RCRA)** taken in conjunction with toxics control and enforcement embodied in the **Water Quality Act** of **1987** are disconcerting to municipalities. **RCRA** regulations now specifically exempt household hazardous wastes from compliance while the **Water Quality Act** does the same - thereby indirectly encouraging small quantity generators to release potentially toxic pollutants to a **POTW** [21] making the **POTW** the toxics treater of last resort.

**EPA's** currently proposed sludge disposal standards set tough new requirements for pathogen and chemical reduction in sewage sludge prior to disposal by one of five options. It, however, leaves the disposal of sewage sludge to municipal landfills as a much more generous option to be controlled under solid waste disposal regulations proposed in 1988. These regulations do not follow the pathway exposure regulation but use containment principles and which will encourage sewage sludge landfills.

Finally **EPA's** recently proposed storm water discharge regulations are likely to affect U.S. municipalities in two ways. First, combined sewer overflows will no longer be permitted as storm water discharges but will require diversion to **POTWs** or in-system treatment under revised **NPDES** permits. Second, municipalities with populations greater than 100,000 probably will be required to develop storm water management plans. These will be used to identify and correct illicit connections and disposal practices associated with storm sewers - obviously the precursor to storm water treatment as set out in the amended **U.S.- Canada Great Lakes Water Quality Agreement.**

## 7. FINDINGS AND COST ESTIMATES

A general review of the U.S. experience together with the MOE 37-plant study and Monteith's work suggests certain priorities in the institution of **BATEA** at municipal sewage works in the Ontario for toxic and hazardous pollutant removal as well as conventional pollution abatement and nutrient control.

I. The immediate implementation of secondary treatment at all **MSTPs** in Ontario not providing for that level of treatment now, or inadequate in capacity to properly provide for it now, is an obvious means of reducing direct toxic discharges to receiving waters from municipal sources. Activated sludge systems having hydraulic retention times in excess of six hours as well as reasonable acclimated mixed liquors will substantially remove toxic material including metals from plant effluents.

**II.** This removal, however, will be at the expense of concentrating the toxics in the sewage sludge except for the **VOCs** which primarily will be volatilized or biodegraded. To protect the quality of the sludge therefore and to reduce the emissions of **VOCs** from the plant, the early introduction of a municipal pretreatment program of the type currently proposed by MOE based on U.S. experience is essential. This ensures that toxicity is primarily contained at the source and that substitution, recycle and reclamation of the offending substances are seriously considered by the industrial discharger. Household toxic and hazardous wastes will continue to be a concern because of their significance in the total plant loading. Public education to limit these discharges must be an ongoing thrust of the control program even though it provides a frustrating and unsatisfying approach.

**III.** Under the foregoing circumstances, it is unlikely that advanced waste water removal will be required in very many instances. Nutrient removal of phosphate and ammonia when required will increase the effectiveness of current secondary treatment plants and where additional toxic removals are justified powdered activated carbon additions may prove to be sufficient to effect any further need for increase in efficiency.

**IV.** Certainly site-specific requirements will eventually (water quality impact assessments) govern the design of effluent permits working from the floor of technology - based standards. Rather than monitor for the effectiveness of specific toxic removals at **MSTPs** on a continuous basis which is time consuming and costly, whole effluent toxicity testing should be introduced. Results from the **WET** program should be interpreted to track toxic discharge offenders.

**V.** Sludge disposal alternatives in light of contained toxic and hazardous materials should be realistically defined, technologically effective and closely regulated and enforced. This is the ultimate depository for toxics and the processes approved must be fully understood and properly managed.

**VI.** The management and operation of **MSTPs** must be maintained at a high level including the training and certification of all levels of participants.

Finally, the issue of cost of service and revenue dependency must be assessed by all waste water utilities. Environment Canada has produced data to indicate that both municipal water and wastewater utilities in Canada do not charge users sufficiently for these service so as to recover costs.

The National Council or Public Works Improvement in the United States stated that *"Artificially low prices for wastewater treatment services can result in excessive demands for treatment, inflated estimates of future needs, and will not provide a sufficient stream of revenue to support new debt or to set aside retained earnings in a reserve for later investment in improved plant or equipment" [10].*

The Ontario Ministry of the Environment made it clear in the ***White Paper*** on *"Controlling Industrial Discharges to Sewers" [4] "that operating costs for the sewer use control program be funded locally under a user pay basis".* The Ministry indicated that *"whichever financial scheme (user pay) has been chosen finally, it is imperative that it be adopted by all municipalities in order to provide a province-wide consistency".*

Current estimates of water and waste water service charges in Ontario prepared by the writer indicate that the median per capita charge for residential water and sewer service in Ontario is $70 per year while the actual cost on a residential basis for providing the combined service was $95.00 per capita per year.

To establish revenue dependency therefore a $25.00 increase in per capita residential charges would be required over current levies.

Environment Ontario also indicates that a municipal pretreatment program without subsidy would cost about three dollars per capita annually to institute and operate.

Other studies have revealed the need to increase the charge in the order of $25.00 per capita per year to properly accommodate badly needed rehabilitated programs for water supply and wastewater systems [22].

Improved waste water treatment to meet **MISA** standards are unlikely to require major outlays in the average Ontario municipality. Estimates of $25.00 per capita per year have been prepared as reasonable which actually represents costs associated with upgrading the level of treatment in 29 primary MSTPs.

The provision of control of combined sewer overflows, however, brings forward major spending forecasts that could range from $25.00 to $200.00 per capita per year based on studies done for the Toronto and Hamilton areas.

Indeed if the total cost of improvements in water and sewage works services in Ontario municipalities were considered it might be tabulated on the following annual per capita cost basis. These costs are inclusive of annual fixed charges with financing over 20 years at 11 percent interest plus annual operating costs.

| | CURRENT CHARGES | COSTS |
|---|---|---|
| **Water And Sewage Works Service** | $ 60 | $ 95 |
| **MISA Pretreatment** | - | 3 |
| **Rehabilitation - Additional** | 10 | 35 |
| **MISA MSTP Improvements** | - | 25 |
| **CSO Control** | | 62 |
| **Total** | $ 70 | $ 220 |

So that if municipalities were to adopt a full cost of service approach to providing environmental services and senior governments eventually were to withdraw subsidies, the actual charges per resident could equal at least $200.00 per annum. The attached **Table VIII** provides U.S. data indicating the real costs of environmental services at $480.00 Canadian per household or $360.00 per household for water and sewage works service. This represents approximately $110.00 per capita per year at current levels of service increasing with improved levels of service, **BATEA**, rehabilitation and CSO control but not storm water management) to $150.00 Canadian per capita per year based on **Table IX.** [22]

Since the American program in environmental service improvement is ahead of the Ontario program, there is a reasonable congruence in the estimated future costs of both programs. These approximate estimates would therefore indicate the cost of water and sewage works services per resident in Ontario will increase by at least three times when the indicated improvements in the control of toxics in surface waters are reasonably complete (no estimates have been provided for future storm waster management). It is assumed that over this same time frame, government subsidies will be phased out.

The establishment of full cost pricing of universally metered customers will be essential to this program to:-

- permit restoration of all systems before a staggering replacement cost becomes a reality;
- provide for the future improvements on a budgeted basis;
- reduce the fiscal pressures on federal and provincial budgets;
- conserve on water use and thereby reduce pollution;
- ease demands on the physical capacities of water and sewage works;
- permit fair and equitable pricing among consumer types;
- permit consumers to act in a responsible and conservative manner with regard to a sustainable development.

**N. B.** Annual payments of principal and interest on a capital outlay of $ 1,000,000 using a 20 year financing at 11 percent interest represents $ 125,600 per year over 20 years.

# REFERENCES

1. D. MacKay - **"DRASTIC ACTION NEEDED TO PROTECT CANADA'S WATER RESOURCES"** - Environmental, Science and Engineering, Vol.2, No.1, February 1989.

2. International Joint Commission - **"REVISED GREAT LAKES WATER QUALITY AGREEMENT OF 1978 AS AMENDED BY PROTOCOL"** signed November 18, 1987.

3. Ontario Ministry of the Environment - Municipal and Industrial Strategy for Abatement - **"A POLICY PROGRAM STATEMENT OF THE GOVERNMENT OF ONTARIO ON CONTROLLING MUNICIPAL AND INDUSTRIAL DISCHARGES TO SURFACE WATERS"** - June 1986.

4. Ontario Ministry of the Environment - **"CONTROLLING INDUSTRIAL DISCHARGES TO SEWERS (MISA)"** - September 1988.

5. Ontario Ministry of the Environment. Thirty Seven Municipal Water Pollution Control Plants - **"PILOT MONITORING STUDY - VOL. I & II"** - December 1988.

6. S.A. Hannah, B.M. Austern, A.E. Erlap and R.A. Dobbs - **"REMOVAL OF ORGANIC POLLUTANTS BY TRICKLING FILTER AND ACTIVATED SLUDGE"** - Journal WPCF, Vol 60, No.7, 1988.

7. E. Namkung, and B.E. Rittman - **"ESTIMATING VOLATILE ORGANIC COMPOUND EMISSIONS FROM PUBLICLY-OWNED TREATMENT WORKS"** - Journal WPCF, Vol.59, No.7, 1987.

8. Lester J.N. - **"HEAVY METALS IN WASTEWATER AND SLUDGE TREATMENT"** - CRC Press, Boca Raton, Fla. [1988].

9. Dietrich M.J. et al - **"REMOVAL OF POLLUTANTS FROM DILUTE WASTE WATER BY THE PACT"** Environ. Prog. 7, 143 [1988].

10. National Council on Public Works Improvement **"WASTEWATER MANAGEMENT: CURRENT POLICIES AND FUTURE OPTIONS"** Washington D.C., May 1987.

11. Evans B. and Filman D. - **"SOLIDS HANDLING COSTS AT LARGE SEWAGE TREATMENT PLANTS"**, Environ. Eng. Proc. 1988, Specialty Conference Can. Soc. Civil Eng. - ASCE, Vancouver, B.C., 1988.

12. Interview with Rebecca Hammer, EPA - **"A CHALLENGE FOR A NEW ADMINISTRATION"** - Journal of WPCF, Vol.60, No.12, December 1988.

13. U.S. EPA **"1986 NEEDS SURVEY REPORT TO CONGRESS: AN ASSESSMENT OF NEEDED POTW FACILITIES IN THE UNITED STATES"**.

14. U.S. EPA - **"CODE OF FEDERAL REGULATION PART 133 - SECONDARY TREATMENT"** - 1988 edition.

15. U.S. Federal Register 49, 46 - **"DEVELOPMENT OF WATER QUALITY - BASED PERMIT LIMITATIONS FOR TOXIC POLLUTANTS: National Policy"** [1984].

16. U.S. EPA - **"CODE OF FEDERAL REGISTER PART 403 - EPA PRETREATMENT STANDARDS"** - 1987.

17. U.S. EPA - Office of Water Regulations and Standards - **"REPORT TO CONGRESS ON THE DISCHARGE OF HAZARDOUS WASTES TO POTWs"**, February 1986.

18. D. Morse - **"SLUDGE IN THE NINETIES"** - Civil Engineering American Society of Civil Engineers, August 1989.

19. Water Pollution Control Federation - **"REVIEW OF EPA SEWAGE SLUDGE TECHNICAL REGULATIONS"** - Journal WPCF, Vol.61, No.7, July 1989.

20. Roger Truith - **"EPA's CARROT TURNS INTO A BIG STICK"** - Water Engineering & Management - July 1989.

21. J.T. Egan, POTWs and EPA: **"A PARTNERSHIP FOR THE FUTURE"** - Journal, WPCF Vol. 61, No. 2, February 1989.

22. U.S. EPA - Municipalities, Small Business and Agriculture - **"THE CHALLENGE OF MEETING ENVIRONMENTAL RESPONSIBILITIES"** - September 1988.

23. Ontario Ministry of The Environment - **"WATER DISTRIBUTION AND SEWERAGE REHABILITATION PROGRAM FOR ONTARIO MUNICIPALITIES"** - June 30, 1983

TABLE I - 37 PLANT PILOT MONITORING STUDY
TOXIC PRESENCE & REDUCTION
APPROXIMATIONS

| POLLUTANT | RAW SEWAGE | | | | | SECONDARY EFFLUENT | | | | | RAW & TREATED SLUDGE | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unit | Freq. Det. % | Plant Det. # | Geo. Mean | Max. | Freq. Det. % | Plant Det. # | Geo. Mean | Max. | Reduct. % | Freq. Det. % | Plant. Det. # | Geo. Mean Raw | Geo. Mean Treat | Reduct. % |
| CONVENTIONAL | | | | | | | | | | | | | | | |
| Dis. Organic Carbon (DOC) | mg/L | 100 | all | 22 | 184 | 100 | all(28) | 8 | 297 | 60 | 100 | all | 60600 | - | - |
| Total Nitrogen (N) | " | " | all | 25 | 76 | " | " | 8 | 32 | 68 | 100 | all | 36900 | 38500 | nil |
| Phosphorus (total) | " | " | 30 | 5 | 18 | 98 | 24 | 0.68 | 5.5 | 86 | " | " | 20350 | 76630 | - |
| Ammonia (NH3-N) | " | " | all | 15 | 43 | 91.5 | all | 3.9 | 28 | 74 | " | " | 5911 | 17658 | - |
| BOD-5 day | " | " | all | 140 | 802 | 100 | " | 21.2 | 120 | 86 | - | - | - | - | - |
| Phenolics (4AAP) | " | 13.5 | 14 | 0.31 | 16 | 15 | 15 | 0.07 | 0.68 | 78 | 82 | 29 | 82 | 43 | 47 |
| METALS (15) | | | | | | | | | | | | | | | |
| Strontium (high) | ug/L | 100 | all | 371 | 2250 | 100 | all | 341 | 4500 | 8 | 100 | all | 231 | 241 | - |
| Aluminum (high) | " | 95 | 36 | 1000 | 22960 | 74 | " | 102 | 5800 | 90 | 100 | all | 102041 | 10715 | - |
| Mercury (low) | " | 97 | all | 0.23 | 1.6 | 95 | " | 0.03 | 0.36 | 37 | 100 | 33 | 2.23 | 3.24 | - |
| Cyanide (low) | " | 30 | 12 | 1.9 | 19000 | 19 | 13 | 1.3 | 43 | 32 | 7.5 | 3 | 0.02 | - | - |
| Others (11) | " | 1-99 | 1-37 | 6.5-211 | 5300 | 1-98 | 1-28 | 2.1-53 | 1400 | 64-88 | 4-100 | 1-34 | 0.5-9800 | 0.5-989 | - |
| BASE NEUTRAL & ACID EXTRACT CMPDS. (31) | | | | | | | | | | | | | | | |
| Pentachlorophenol (PCP) | ug/L | 1.8 | 4 | 12.94 | 121 | 1.3 | 2 | 2.71 | 58.7 | 78 | - | - | - | - | - |
| Others | " | 0.4-60 | 1-32 | 5.05-26 | 784 | 0.4-3.1 | 1-4 | 1.07-2.7 | 143 | 68-93 | 2-30 | 347 | 2900-7300 | 1300-2220 | - |
| DIOXINS & FURANS (3) | | | | | | | | | | | | | | | |
| All (3) | ng/L | 1.9-7. | 1-4 | 0.41-0.87 | 28.0 | 2.3-9.1 | 1-4 | 0.15-0.38 | 11.0 | 64-81 | 2-50 | 1-20 | 2.4-8.5 | 2.5-7.1 | - |
| PESTICIDES, HERBICIDES, PCB'S (29) | | | | | | | | | | | | | | | |
| PCB's | ug/L | 15.2 | 17 | 0.06 | 2.31 | 4.0 | 8 | 0.02 | 0.19 | 67 | 78.0 | 27 | 88.7 | 114.1 | - |
| Others (28) | " | 0.4-77 | 1-37 | 0.01-0.13 | 5.9 | 0.4-78 | 1-28 | 0.08-0.01 | 34 | 0-85 | 3.9-78 | 2-27 | 4-88 | 3.7-114 | - |
| VOLATILES (17) | | | | | | | | | | | | | | | |
| Chlorobenzene | ug/L | 0.5 | 1 | 20.05 | 42 | 0.5 | 1 | 1.0 | 2.1 | 95 | - | - | - | - | - |
| Others (16) | " | 0.5-16 | 1-14 | 20-26 | 9800 | 0.5-8 | 1-9 | 1.0-10.0 | 84 | 95-100 | 2.0-31 | 1-14 | 641-1346 | 261-816 | - |

## TABLE II

### Removal of volatile organic pollutants

| Pollutants | Activated sludge<br>Percent removal | o |
|---|---|---|
| Carbon Tetrachloride | 81 | 22 |
| 1,1 Dichloroethane | 97 | 2 |
| 1,1 Dichloroethylene | > 97 | -- |
| Chloroform | 98 | 3 |
| 1,2 Dichloroethane | 95 | 5 |
| Bromoform | 68 | 22 |
| Ethylbenzene | > 98 | -- |
| Average removal of all volatiles | > 91 | -- |

### Removal of semivolatile organic pollutants

| Pollutants | Activated sludge<br>Percent removal | o |
|---|---|---|
| Bis(2-ethylhexyl)phthalate | 71 | 19 |
| Dibutylpthalate | 71 | 19 |
| Naphthalene | 95 | 3 |
| Phenanthrene | 93 | 4 |
| Pyrene | 91 | 5 |
| Fluoranthene | 92 | 4 |
| Isophorone | 96 | 2 |
| Bis(2-chloroethyl)ether | 64 | 38 |
| p-Dichlorobenzene | 94 | 5 |
| Phenol | 91 | 8 |
| 2,4 Dichlorophenol | 86 | 20 |
| Pentachlorophenol | 60 | 36 |
| Lindane | 57 | 37 |
| Heptachlor | 67 | 13 |

**Reference 6**

o - standard deviation

## T A B L E III

## Comparison of organic pollutant removals by two activated sludge systems

| Pollutants | Activated sludge this study percent removal | Activated sludge this study o | Activated sludge previous study percent removal | Activated sludge previous study o | Differences in percent removals, (this study)–(previous study) |
|---|---|---|---|---|---|
| Carbon Tetrachloride | 81 | 22 | 74 | 22 | +7 |
| 1,1 Dichloroethane | 97 | 2 | 94 | 2 | +3 |
| 1,1 Dichloroethylene | > 97 | -- | 92 | 7 | >+5 |
| Chloroform | 98 | 3 | 86 | 9 | +12 |
| 1,2 Dichloroethane | 95 | 5 | 84 | 10 | +11 |
| Bromoform | 68 | 22 | 65 | 14 | +3 |
| Ethylbenzene | > 98 | -- | 93 | 13 | >+5 |
| Bis(2-ethylhexyl)phthalate | 71 | 19 | 87 | 16 | -16 |
| Dibutylphthalate | 91 | 6 | 88 | 17 | +3 |
| Naphthalene | 95 | 3 | 97 | 1 | -2 |
| Phenanthrene | 93 | 4 | 95 | 2 | -2 |
| Pyrene | 91 | 5 | 95 | 2 | -4 |
| Fluoranthene | 92 | 4 | 95 | 2 | -3 |
| Isophorone | 96 | 2 | 98 | 1 | -2 |
| Bis(2-chloroethyl)ether | 64 | 38 | 80 | 31 | -16 |
| p-Dichlorobenzene | 94 | 5 | 94 | 3 | 0 |
| Phenol | 91 | 8 | 86 | 9 | +5 |
| 2,4 Dichlorophenol | 86 | 20 | 99 | 1 | -13 |
| Pentachlorophenol | 60 | 36 | 96 | 2 | -36 |
| Lindane | 57 | 37 | 18 | 16 | +39 |
| Heptachlor | 67 | 13 | 65 | 3 | +2 |

**Reference 6**

o - standard deviation

## TABLE IV

### Average concentrations (ug/L unless indicated) of VOCs in influent and effluent at the Calumet and West-southwest WWTPs

| | Compound | Calumet | | West-southwest | |
|---|---|---|---|---|---|
| | | Influent | Effluent | Influent | Effluent |
| (1) | Benzene | 23.3±21.3[a] | BDL[b] | 0.43±0.75 | BDL |
| (2) | Chlorobenzene | 0.47±0.81 | BDL | BDL | BDL |
| (3) | Chloroform | 4.0±0.78 | 7.07±8.86[c] | 4.4±1.31 | 2.4±0.26 |
| (4) | 1,2-Dichloroethane | 1.07±1.85 | BDL | 0.63±1.10 | BDL |
| (5) | Ethylbenzene | 17.7±9.44 | 0.5±0.87 | 10.4±7.15 | BDL |
| (6) | Methylene Chloride | 9.77±9.09 | 11.41±12.9[c] | 48.3±58.92 | 10.8±15.22 |
| (7) | Tetrachloroethylene | 16.13±16.63 | 2.1±0.9 | 12.2±8.52 | 1.6±1.71 |
| (8) | Toluene | 85.47±62.38 | 6.2±10.69 | 21.8±5.32 | BDL |
| (9) | 1,2-Trans-Dichloroethylene | 1.43±1.63 | BDL | 1.77±0.34 | BDL |
| (10) | 1,1,1-Trichloroethane | 12.77±7.64 | 2.9±1.85 | 14.7±4.0 | 2.2±0.53 |
| (11) | Trichloroethylene | 9.7±9.22 | 0.5±0.87 | 22.3±27.72 | 2.1±0.46 |
| Total VOC concentration | | 181.8±140.8 | 33.4±35.45 | 136.9±115.13 | 19.1±18.18 |
| Annual VOC loads, T/a | | 57.5 | 10.6 | 158.1 | 22.1 |
| Actual VOC removal | | 81.6% | | 86.0% | |

Reference 7

[a] - indicates mean values with standard deviation
[b] - BDL indicates below detection limit
[c] - indicates conditions where effluent concentration exceeds influent

## T A B L E V

## Best estimates of VOC removals by all three mechanisms at the Calumet WWTP

| Compound | | Predicted % VOC removal by each mechansim | | | |
|---|---|---|---|---|---|
| | | Volatilization | Adsorption | Biodegradation | Total |
| (1) | Benzene | 2.6% | 0.1% | 94.8% | 97.5% |
| (2) | Chlorobenzene | 2.3% | 0.1% | 95.1% | 97.5% |
| (3) | Chloroform | 43.6% | 0.2% | --[a] | 43.8% |
| (4) | 1,2-Dichloroethane | 20.0% | 0.1% | -- | 20.1% |
| (5) | Ethylbenzene | 3.2% | 0.1% | 94.1% | 97.5% |
| (6) | Methylene Chloride | 1.5% | 0.0% | 96.0% | 97.5% |
| (7) | Tetrachloroethylene | 83.6% | 0.4% | -- | 84.0% |
| (8) | Toluene | 3.2% | 0.1% | 94.2% | 97.5% |
| (9) | 1,2-Trans-Dichloroethane | 56.5% | 0.0% | -- | 56.5% |
| (10) | 1,1,1-Trichloroethane | 44.9% | 0.3% | -- | 45.2% |
| (11) | Trichloroethylene | 69.% | 0.2% | -- | 69.6% |
| **Total percent removal** | | **18.1%** | **0.1%** | **71.0%** | **89.2%** |
| **Total VOC removed, T/a** | | **10.39** | **0.06** | **40.85** | **51.30** |
| **Total Input VOC Load** | | | | | **57.5 T/a** |
| **Total VOC removal = (51.2965/57.5)x100% = 89.2%** | | | | | |

**Reference 7**

[a] **Indicates that VOC is not biodegradable under aerobic conditions.**

## TABLE VI

## YARDSTICKS

| Pollutants | Land Application | Distribution & Marketing | Monofills and Surface Disosal | Incineration |
|---|---|---|---|---|
| Aldrin | • | • | | |
| Arsenic | • | • | • | • |
| Benzene | | | • | |
| Benzo(a)pyrene | • | • | • | |
| Beryllium | | | | • |
| Bis (2-ethyl-hexyl) phthalate | | | • | |
| Cadmium | • | • | • | • |
| Chlordane | • | • | • | |
| Chromium | • | • | | • |
| Copper | • | • | • | |
| DDD, DDE, DDT | • | • | • | |
| Dieldrin | • | • | | |
| Dimethyl nitrosamine | • | | • | |
| Heptachlor | • | • | | |
| Hexachlorobenzene | • | • | | |
| Hexachlorobutadiene | • | • | | |
| Lead | • | • | • | • |
| Lindane | • | • | • | |
| Mercury | • | • | • | • |
| Molybdenum | • | | | |
| Nickel | • | • | • | • |
| PCB | • | • | • | |
| Selenium | • | • | | |
| Toxaphene | • | • | • | |
| Trichloroethylene | • | | • | |
| Total Hydrocarbons | | | | • |
| Zinc | • | • | | |

In the proposed regulations, 27 sludge contaminants will be regulated over five disposal options. Source is Black & Veatch Residuals Management Group.

Reference 18

## TABLE VII

### Non-agricultural land pollutant limits

| Pollutant | Maximum sewage sludge concentration, [a](mg/kg) |
|---|---|
| Aldrin/dieldrin | 0.33 |
| Arsenic | 36 |
| Benzo (a) pyrene | 6.9 |
| Cadmium | 380 |
| Chlordane | 24 |
| Chromium | 3100 |
| Copper | 3300 |
| DDT/DDE/DDD (total)[b] | 0.11 |
| Dimethyl nitrosamine | 1.4 |
| Heptachlor | 1.5 |
| Hexachlorobenzene | 2.8 |
| Hexachlorobutadiene | 6.8 |
| Lead | 1600 |
| Lindane | 92 |
| Mercury | 30 |
| Molybdenum | 230 |
| Nickel | 990 |
| Polychlorinated biphenyls | 0.11 |
| Selenium | 64 |
| Toxaphene | 0.97 |
| Trichloroethylene | 180 |
| Zinc | 8600 |

**Reference 19**

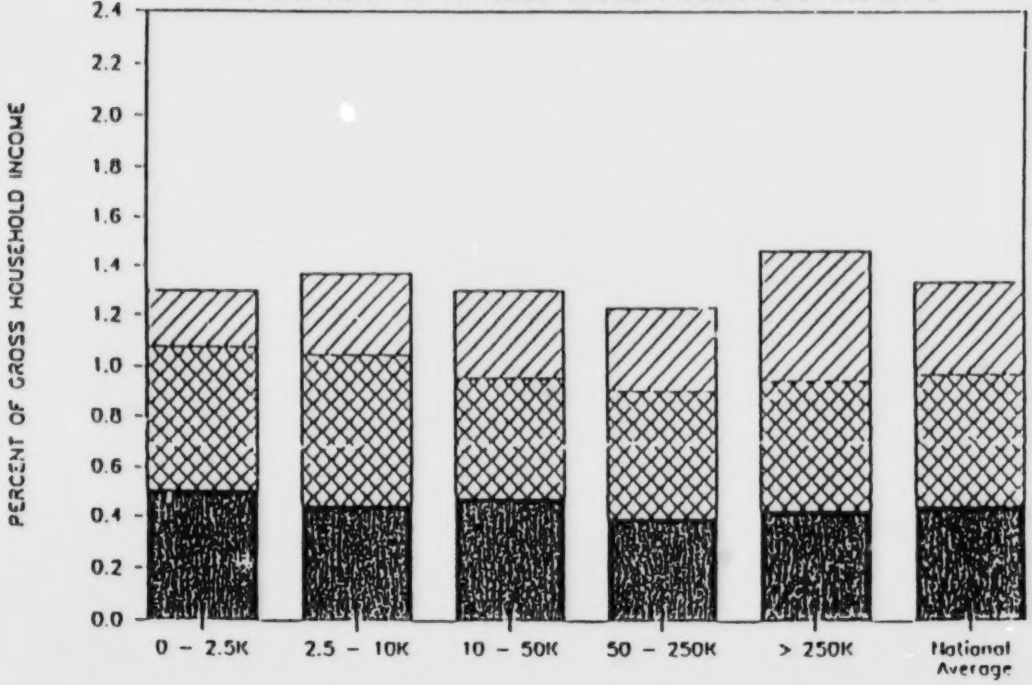
[a] -dry weight basis

[b] -DDT-2,2-Bis(chlorophenyl)-I,I,I-trichlorethane
DDE-1,1-Bis(chlorophenyl)-2,2-dichloroethane
DDO-1,1-Bis(chlorophenyl)2,2-dichloroethane

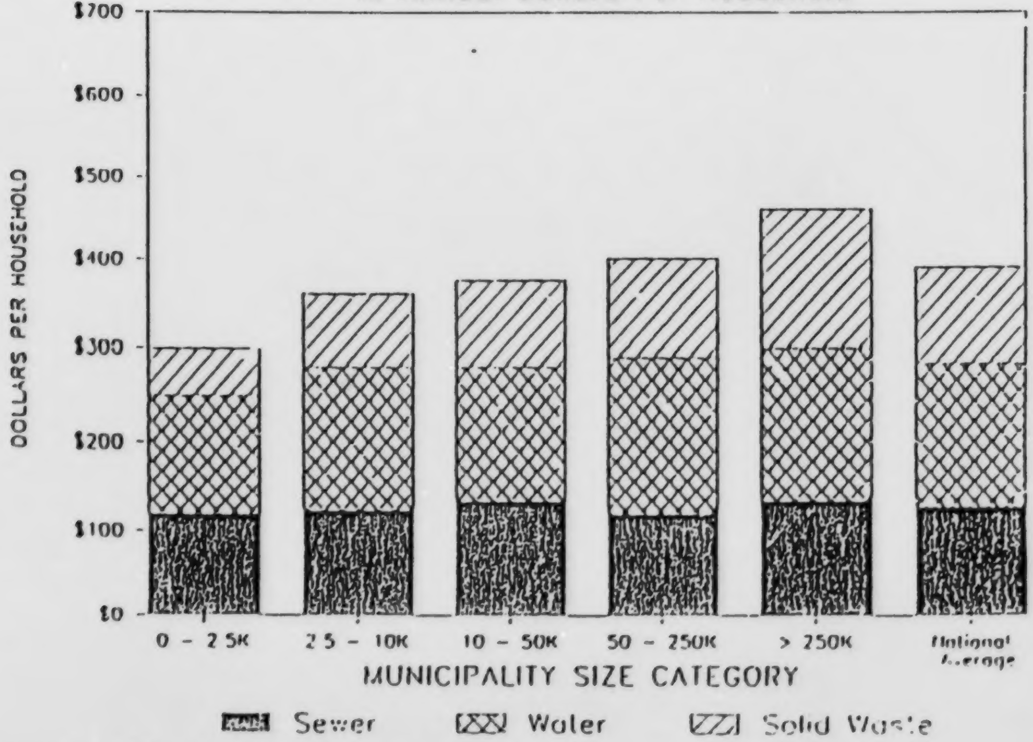
## TABLE VIII.

## CURRENT AVERAGE ANNUAL HOUSEHOLD COSTS FOR ENVIRONMENTAL SERVICES

### I. Percent of Annual Gross Household Income



### II. Annual Dollars Per Household



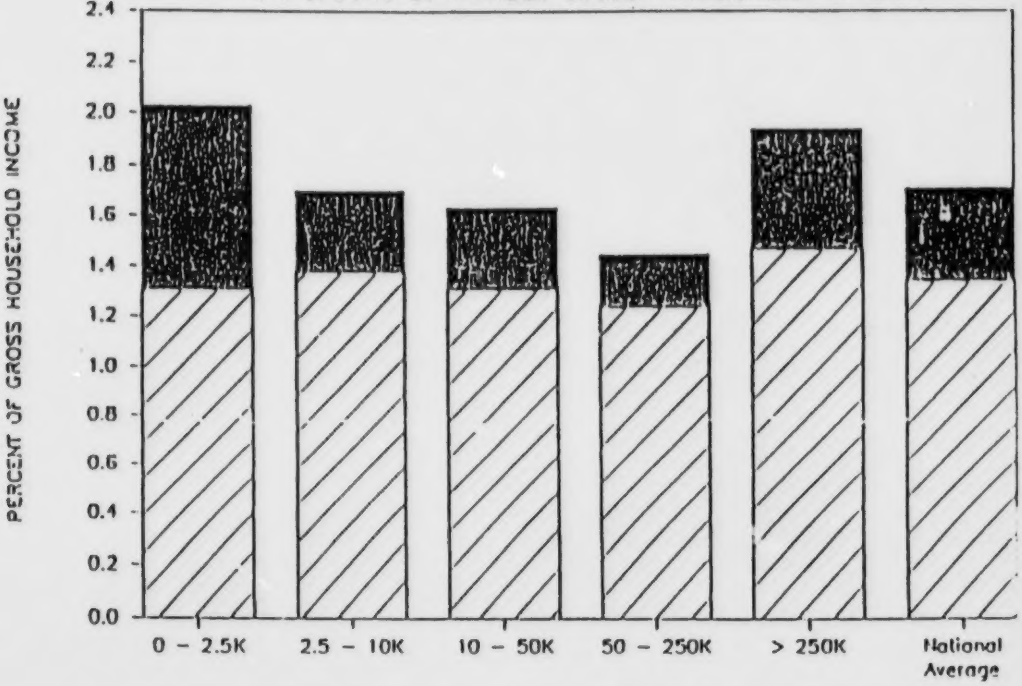
Source: Municipal Sector Study Database

Reference 21

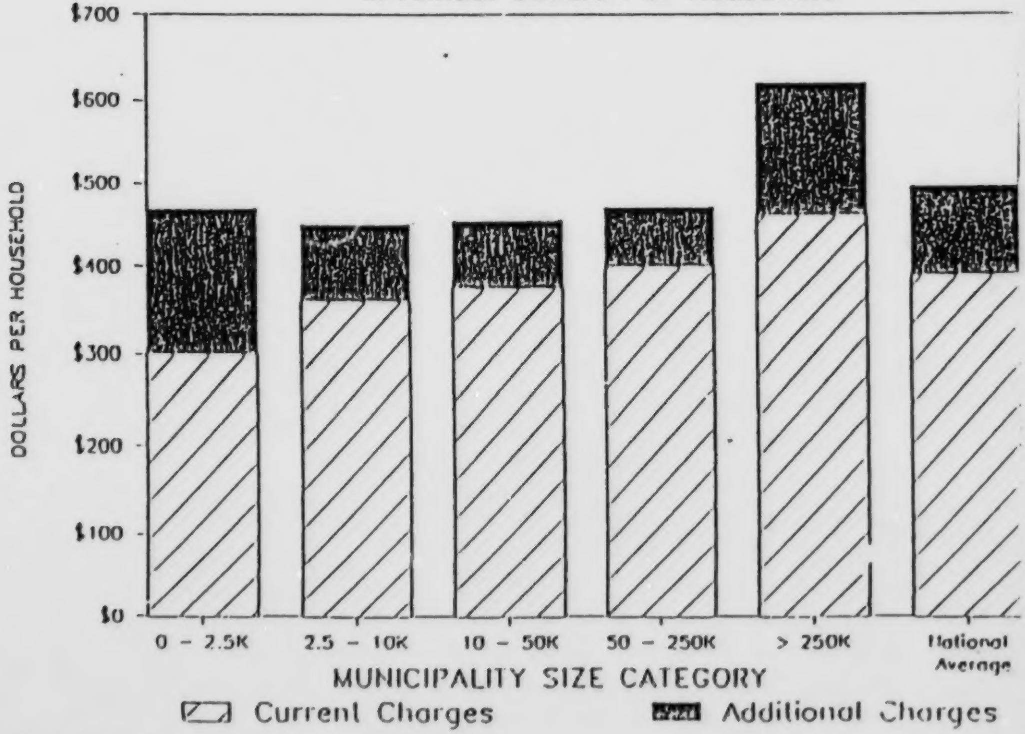
TABLE IX

## CURRENT AND POTENTIAL ADDITIONAL AVERAGE ANNUA HOUSEHOLD COSTS FOR IMPROVED ENVIRONMENTAL SERVI

I. Percent of Annual Gross Household Income



II. Annual Dollars Per Household



Source: Municipal Sector Study Database

Reference 21

# LEGAL IMPLICATIONS OF SEWER USE PROGRAM

Metro Patel,
Ontario Ministry of the
Environment,
Legal Services Branch

## ABSTRACT

Municipalities that have adopted or will be adopting the Model Sewer Use Program By-Law will have completed some of the basic requirements for implementing the Sewer Use Program. Mr. Patel examined both the Model Sewer Use By-Law and the legal consideration in the development and implementation of the Sewer Use Program.

# CONTROLLING QUALITY IN THE ANALYTICAL LABORATORY

Donald E. King, M.Sc
Quality Assurance Officer
Laboratory Services Branch
Ontario Ministry of the Environment

## INTRODUCTION

Analytical measurement results are often perceived to be fixed values 'written in stone'. In reality, there is an inherent range of uncertainty associated with all measurement results. In addition there is a potential risk of error. This error may affect only a single result, or it may bias the average of several results. It is the function of the laboratory quality assurance program to reduce the risk of error that will significantly affect the interpretation of measurement data.

This paper discusses the way in which the analyst, the method, the instrument device, and the sample interact to affect data quality and data interpretation. It also discusses the components of a comprehensive control program to minimize the impact of error, and the need for an overall quality management program.

## CONTROLLING QUALITY IN THE MEASUREMENT PROCESS

Analytical science in the environmental laboratory involves the constant interplay of samples, methodology, facilities, equipment and supplies, and people. The management of quality in this setting requires development and implementation of well-documented policies, guidelines, protocols and procedures. It also requires a clear understanding of the sources of variability and error, and the mechanisms available to monitor and control them.

Quality implies suitability for use. Data quality is frequently discussed in terms of precision (the spread of the data about a central value) and accuracy (the closeness of the central value to a true or predefined value). Both terms have several meanings dependent on context.

known short-term (single analyst, within-batch) variability of the method. Control requires a clear understanding of the capabilities and deficiencies of the system being controlled. It involves the development of performance specifications, a reliable mechanism for monitoring the system, and defined protocols to ensure problem identification and appropriate remedial action.

## Method Control

Method control starts with comprehensive documentation of all operations and procedures within the total method. Critical components must be identified and appropriate control checks must be defined, including the action to be taken when deficiencies are detected.

Standard methods must be shown to be appropriate to the intended use. The competent analyst will verify that matrix effects are minimal, and that the method is reliable. Comparisons between methods and analysts will help to create confidence in the method, and to establish control limits for calibration, method recovery, analyst repeatability, blank variability, and related control factors.

## Supply Control

The specification of reagent and labwares quality requirements must be followed up by protocols to ensure that these specifications are recognized and implemented by purchasing agents. Whenever possible, the quality of supplies should be verified on receipt rather than waiting until they need to be placed into service.

## Equipment Control

The stability and reliability of laboratory appliances, equipment and instrumentation, must be established and ensured by a regular maintenance and verification program.

## Technique Control

The proper implementation of a method requires properly trained and experienced staff. Appropriate educational pre-requisites do not substitute for the need to verify that proper procedure will be followed. Training in control philosophy and techniques has not received the attention it deserves. The supervisor must be made accountable for demonstrating that staff follow all analytical and quality assurance practices as defined.

## Accuracy Control

Accuracy derives from calibration using standards traceable to internationally recognized reference standards. In a general sense it also derives from the use of officially sanctioned methodology. It is well known however that methodologies based on different chemical or physical principles are often biased when used on sample types for which they were not originally devised.

The 'overall accuracy' of a method depends on the controlled use of reference standards for the purpose of calibrating the measurement device, and on the use of certified reference materials for determining the efficiency of the method. Having established these 'calibrations' one then uses in-house standards and control materials on a daily basis to assess the need to correct for apparent changes in device response or method recovery. Proper control technique will permit both to vary from day to day within defined limits.

## Calibration/Recovery Control

The automatic use of standards to correct for perceived changes in recovery or calibration will cause systematic error in all results calculated using that correction.

Every analytical batch should be accompanied by one or more control standards and samples. These are measured and compared against predefined limits to determine the acceptability of the analytical results for that batch.

Precision control requires the analyst to stop an analytical process, or to delay the release of results, whenever a single control result exceeds the specified limits relative to its predetermined value. Control limits for individual values are often set at three times the analytical standard deviation.

Bias control requires the analyst to identify and forestall trends in the average result of a control sample over time. Control limits for an average of nine results will be three times tighter than the control limits for a single result. In other words, an average calculated from nine sequential control results should not drift from the expected value by more than one standard deviation.

## Laboratory Environment Control

Analytical measurements are subject to chronic and random sources of contamination from the laboratory environment. Organic solvents and dust particles, 'dirty fingers', improperly cleaned glassware, and sample contact with materials in the analytical equipment, are but a few sources of error.

Chronic stable levels of contamination can be estimated by use of laboratory blanks, and if the effect is controlled, these blanks can be used to correct analytical results.

Sporadic, random sources of contamination will be revealed by gross unpredictable variation in the laboratory blank, or in the results of duplicate analysis of selected samples. Great care must be taken in using blank data to correct analytical results under such conditions.

## Sample Control

Sample matrix components can affect method recovery, interfere with the identification of the analyte, or interfere with the detection and measurement steps. Analytical methods must therefore be demonstrated to be effective for use on the type of sample being submitted.

The analyst must advise the data user when there is concern that the selected or routine method may not be appropriate for specific or atypical samples.

## Performance Control

Overall performance control will include;
- control standards to verify proper standardization
- method blanks to verify corrections for 'zero',
- control samples to verify method recovery,
- spiked samples to evaluate sample matrix effects,
- internal and surrogate standards to evaluate method performance on a sample by sample basis
- duplicate analysis (total method).

The need for, and frequency of such checks will depend on the specific methodology and its known performance characteristics.

### Data Quality Interpretation

Most routine analytical results are based on a single analysis only. The reliability of the result is inferred from instrumental stability and calibration control data, method repeatability and recovery control data, apparent suitability of the sample and the likelihood of matrix effects, the relationship to other known information (other results, sample source, etc.), and overall control of the laboratory environment, including sample preservation, storage, and delay before initiating analysis.

While the analyst may be concerned that the results look unusual, care must be taken not to censor data on this basis alone. There may be other information known to the sampler or project manager which explains the observed result. Suspect results should be withdrawn when a known control problem is identified. When there appears to be no systematic control problem, or when the reliability of the sample is questioned, the data should be reported to the person responsible for data compilation and interpretation, accompanied by appropriate remark codes or text.

## AUDITS

The analyst is ultimately accountable for the quality of data and for the proper identification of suspect data. Laboratory control information operates at two levels: to identify and resolve problems before they impact data quality, and to document the level of quality achieved. The laboratory must be prepared to present this information on the request of a client or other external auditor.

To enhance the apparent quality of data, laboratories should participate in external performance evaluation samples, and in studies of method and interlaboratory comparability. The proper use of such information will help to identify imprecision, bias, or erratic performance, and will promote self-improvement.

## PERFORMANCE MANAGEMENT IN THE LABORATORY

A comprehensive approach to quality assurance in the modern laboratory involves much more than bench level quality control checks discussed above. Laboratory management is responsible for fostering a work environment which encourages the identification and resolution of deficiencies. There must be visible committment to the need for a clearly documented and established quality program. Management of quality implies management of resources to ensure and verify that they will provide the level of service required. There must be a clear understanding of the interplay of people, methodology, facilities, equipment, and supplies, and of the importance of well-documented policies, guidelines, protocols and procedures. Finally, analytical data, and associated records, must be reported and archived in such a way that the quality of the data is known and traceable.

A properly functioning quality management program must ensure that everyone knows and understands their role in assuring data quality. A control program must and will identify problems. A positive supportive response from management will ensure that these problems are resolved, and that they do not impact on the quality of data released.

# VARIABILITY OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WATER POLLUTION CONTROL PLANT INFLUENTS AND EFFLUENTS

Stephen G. Nutt
CH2M HILL ENGINEERING LTD.
Suite 600, 180 King St. S.
Waterloo, Ontario
N2J 1P8

## INTRODUCTION

Over the past decade, regulatory authorities have focussed increasingly upon the control of toxic trace contaminants in treated effluents. Municipal sewage treatment plants (STPs) depend to a large extent on biological processes and were designed to remove conventional contaminants such as BOD and suspended solids. Research has shown that these biological systems can also achieve a high degree of trace contaminant control when operated under stable conditions and after the microbial biomass has acclimated to the contaminants present in the wastewater(1). During the operation of full scale STPs, however, the biological processes may be exposed to highly variable input loadings of a wide range of trace contaminants. The tolerance and dynamic response of the biological processes to such transient conditions is presently unknown. A comprehensive literature search(2) indicated that little information exists with respect to dynamic fluctuations of trace contaminant concentrations in STPs. Most reported data are concerned with metal fluctuations in influent samples. Based on data derived from composited samples, the variability of trace contaminant concentrations in effluents relative to the mean appears to be as great as the relative variability in influents.

An improved understanding of the dynamics of industrial discharges to STPs and the response of treatment processes to variable input conditions will assist regulatory authorities in the management of trace contaminants. Accordingly, the development of a management strategy for the control of trace contaminants in STP effluents was initiated at Environment Canada's Wastewater Technology Centre. This paper reports on an investigation to measure the variability of trace contaminants at three full scale STPs in Ontario. The data from the intensive sampling at these three STPs are also compared to the results of broader-based sampling conducted at thirty-seven Ontario STPs in 1987 under the MISA program(3).

## PROCEDURES

Variability Study. The three STPs that were selected for the variability study were all conventional activated sludge plants. Selection was based on the degree and type of industrial wastewater contribution, ranging from an STP receiving primarily domestic or institutional wastewater to one receiving a high proportion of industrial wastewater. All were of approximately the same design flow rate: Waterloo and Welland at 45,460 $m^3$/d, and Galt at 36,640 $m^3$/d. Waterloo was considered to receive relatively little industrial load. Major contributors included beverage industries, a textile plant, two metal platers and two universities. At Galt, there was a diverse industrial contribution with wastewaters from snack food manufacturers, textile plants, foundries, metal platers, and a range of chemical and manufacturing industries. Industrial contributors to the Welland STP were not as diverse as at Galt, consisting of machinery and rubber products manufacturers and a steel rolling mill.

Detailed descriptions of all sampling and analytical procedures have been presented elsewhere(4,5). In brief, degritted influents and non-chlorinated secondary effluents at the three STPs were sampled manually at 2-hr intervals for 8 consecutive days to provide an influent and effluent sequence of approximately 100 paired data points. A small number of trace contaminants were measured to maintain analytical requirements at a manageable level. The list on candidate trace contaminants was based upon those that were most frequently observed in earlier surveys by other researchers(6,7). This included the six commonly found heavy metals, selected polyaromatic hydrocarbons (PAHs), phenolic compounds, and volatile chlorinated and non-chlorinated organic compounds.

MISA Thirty-Seven Plant Study. Detailed descriptions of the sampling and analytical procedures applied during the thirty-seven municipal water pollution control plant pilot monitoring study have been documented elsewhere(3). The sampling program included a broad range of large and small facilities across the province. Primary, secondary and tertiary mechanical plants as well as lagoons were represented. This included the Waterloo WPCP which had also been sampled during the variability study. Table 1 presents a summary of the distribution of plants, by plant type, which were sampled during the MISA pilot monitoring study.

Table 1
DISTRIBUTION OF PLANTS BY PLANT TYPE
INCLUDED IN THE MISA PROGRAM

| Plant Type | Number of Plants |
|---|---|
| Primary | 7 |
| Secondary | 27 |
| Tertiary | 1 |
| Lagoon | 2 |

The sampling program for influents and effluents at each WPCP involved the collection of 24-hour flow-proportioned composite samples daily for five consecutive days. Samples were analyzed for conventional contaminants, metals, cyanide, base-neutral and acid extractable organic compounds, and pesticides and herbicides. Grab samples were collected three times in each 24-hour period and composited for analysis of volatile organic compounds. An additional 5-day composite sample was prepared of influents and effluents for analysis for dioxin-furan compounds. At facilities where an internal recycle (digester supernatant, filtrate, centrate, etc) was returned upstream of the raw sewage sampling point, a separate sample of the recycle stream was collected and analyzed so that the raw sewage concentration data could be corrected for the recycle stream contribution. Final effluent samples were collected after chlorination in plants which were practising chlorination. Seventeen of the 37 WPCPs were sampled on two occasions during the study, once in warm weather and once in cold weather. The other 20 plants were only sampled once.

The MISA pilot monitoring study incorporated a much more extensive analytical program than the variability study. As well, sludges at the 37 WPCPs were sampled and characterized. In this paper, only raw sewage and final effluent concentration data for contaminants which were included in both the variability study and the MISA 37 plant study are presented. Raw sewage data from all 37 facilities are included. Final effluent data for only the 27 secondary treatment facilities are included.

## RESULTS

Variability Study. Contaminant concentration data are presented in three groups: metals (Table 2), aromatic volatiles and total phenolics (Table 3), and chlorinated volatiles (Table 4). Data were included for those trace contaminants that occurred more than 50 percent of the time, except for p,m-xylene which occurred 45 percent of the time only at Welland. Calculated for each contaminant are the geometric mean, the arithmetic mean and the relative standard deviation of influent and effluent concentrations at each of the three STPs. Geometric means are shown in addition to arithmetic means because the arithmetic mean can be biased significantly upwards by as few as one or two very high values as compared to the rest of the values in a data base. This is an important consideration in the analysis of trace contaminant data in wastewater treatment systems since very high concentrations can often occur due to analytical error alone. This will tend to bias the arithmetic mean much more than it would bias the geometric mean of a data set.

---

Table 2
SUMMARY OF TRACE METAL DATA - VARIABILITY STUDY

| | Cadmium | | | Chromium | | | Copper | | | Nickel | | | Lead | | | Zinc | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GM[1] | AM[2] | RSD[3] | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD |
| Waterloo | | | | | | | | | | | | | | | | | | |
| Influent | 4.4 | 4.5 | 24 | 46.7 | 54.2 | 77 | 110 | 122 | 47 | 26.0 | 27.3 | 37 | 13.6 | 20.4 | 99 | 135 | 152 | 51 |
| Effluent | 4.1 | 4.3 | 44 | 27.3 | 29.8 | 50 | 13.5 | 14.3 | 29 | 23.8 | 24.7 | 36 | 5.7 | 6.7 | 110 | 74.9 | 81.4 | 38 |
| Welland | | | | | | | | | | | | | | | | | | |
| Influent | 2.7 | 2.9 | 41 | 14.9 | 16.5 | 56 | 30.9 | 34.1 | 45 | 14.4 | 15.1 | 36 | 8.3 | 12.2 | 130 | 64.9 | 76.2 | 66 |
| Effluent | 2.4 | 2.6 | 35 | 9.1 | 9.3 | 18 | 5.8 | 6.3 | 41 | 13.0 | 13.3 | 19 | 5.3 | 5.6 | 61 | 21.9 | 22.9 | 33 |
| Galt | | | | | | | | | | | | | | | | | | |
| Influent | 3.5 | 6.2 | 160 | 54.3 | 92.8 | 162 | 125 | 146 | 70 | 40.1 | 111 | 495 | 11.1 | 13.9 | 77 | 172 | 199 | 65 |
| Effluent | 2.2 | 2.4 | 50 | 30.1 | 31.8 | 26 | 47.3 | 49.2 | 27 | 48.1 | 66.6 | 102 | 5.3 | 5.4 | 31 | 77.2 | 83.2 | 49 |

[1] Geometric mean for influent and effluent in µg/L.

[2] Arithmetic mean for influent and effluent in µg/L.

[3] Relative standard deviation of influent and effluent mean concentrations, expressed as percent.

### Table 3
### SUMMARY OF TOTAL PHENOLICS AND AROMATIC VOLATILE TRACE ORGANIC DATA - VARIABILITY STUDY

| | Total Phenolics | | | Benzene | | | Toluene | | | p,m-Xylene | | | o-Xylene | | | Ethylbenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GM[1] | AM[2] | RSD[3] | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD |
| **Waterloo** | | | | | | | | | | | | | | | | | | |
| Influent | 16.2 | 20.7 | 60 | 1.4 | 1.7 | 92 | 3.4 | 5.0 | 150 | 8.3 | 50.4 | 680 | 3.2 | 15.2 | 600 | 1.4 | 10.4 | 670 |
| Effluent | 2.7 | 3.3 | 61 | 0.3 | 0.3 | 3 | 0.3 | 0.3 | 50 | 0.3 | 0.4 | 70 | 0.3 | 0.3 | 75 | 0.3 | 0.3 | 9 |
| **Welland** | | | | | | | | | | | | | | | | | | |
| Influent | 9.7 | 12.4 | 67 | Less than 50% Occurrence | | | 0.8 | 1.2 | 150 | 0.6 | 1.2 | 230 | 0.6 | 1.4 | 420 | Less than 50% Occurrence | | |
| Effluent | 2.0 | 2.6 | 81 | | | | 0.3 | 0.3 | - | 0.3 | 0.4 | 120 | 0.3 | 0.3 | 40 | | | |
| **Galt** | | | | | | | | | | | | | | | | | | |
| Influent | 19.9 | 23.6 | 54 | 0.7 | 0.8 | 50 | 4.1 | 9.8 | 220 | 7.5 | 39.6 | 380 | 3.2 | 9.6 | 308 | 1.5 | 7.0 | 390 |
| Effluent | 3.5 | 4.3 | 60 | 0.3 | 0.3 | 30 | 0.3 | 0.3 | 130 | 0.5 | 1.0 | 160 | 0.4 | 0.5 | 100 | 0.3 | 0.4 | 150 |

---

[1] Geometric mean for influent and effluent in µg/L.

[2] Arithmetic mean for influent and effluent in µg/L.

[3] Relative standard deviation of influent and effluent mean concentrations, expressed as percent.

### Table 4
### SUMMARY OF CHLORINATED VOLATILE TRACE ORGANIC DATA - VARIABILITY STUDY

| | Chloroform | | | Trichloroethylene | | | 1,1,1-Trichloroethane | | | Tetrachloroethylene | | | 1,4-Dichlorobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GM[1] | AM[2] | RSD[3] | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD | GM | AM | RSD |
| **Waterloo** | | | | | | | | | | | | | | | |
| Influent | 2.8 | 5.2 | 220 | 1.3 | 1.7 | 88 | 1.1 | 1.4 | 71 | 1.1 | 1.3 | 77 | 1.7 | 2.9 | 100 |
| Effluent | 0.8 | 1.0 | 60 | 0.5 | 0.5 | 40 | 0.6 | 0.7 | 60 | 0.5 | 0.5 | 20 | 0.8 | 0.9 | 30 |
| **Welland** | | | | | | | | | | | | | | | |
| Influent | 3.9 | 5.1 | 73 | Less than 50% Occurrence | | | 1.9 | 2.4 | 74 | Less than 50% Occurrence | | | 2.1 | 2.2 | 30 |
| Effluent | 0.8 | 0.9 | 30 | | | | 1.6 | 2.0 | 67 | | | | 0.8 | 0.9 | 40 |
| **Galt** | | | | | | | | | | | | | | | |
| Influent | 2.2 | 3.3 | 160 | 4.2 | 4.4 | 20 | 5.0 | 5.2 | 23 | 6.9 | 27.7 | 265 | 4.0 | 4.2 | 29 |
| Effluent | 0.9 | 1.0 | 50 | 1.0 | 1.0 | 40 | 2.0 | 2.2 | 36 | 3.3 | 8.6 | 194 | 1.4 | 1.4 | 36 |

---

[1] Geometric mean for influent and effluent in µg/L.

[2] Arithmetic mean for influent and effluent in µg/L.

[3] Relative standard deviation of influent and effluent mean concentrations, expressed as percent.

PAHs were rarely detected at any of the three STPs. With the exception of phenanthrene at the Waterloo STP, PAHs occurred in the influent less than 50 percent of the time and were generally not detected in the effluent. When detected, influent PAH concentrations were less than 5 µg/L. Phenanthrene was detected in 40 percent of the Waterloo influent samples at concentrations ranging from

0.2 to 4.6 µg/L. Corresponding analytical recoveries were approximately 32 percent, based on a spiked surrogate.

For the metal trace contaminants (Table 2), Galt displayed the highest variability as might be expected with the largest industrial contribution of the three STPs. Metal concentrations of up to 1 mg/L were observed in the influent to the Galt STP on several occasions. Effluent metal variability was lower than the influent variability in most cases. Mean concentrations for copper and cadmium in the three plants were similar to those reported by other surveys of full scale STPs, but they were much lower for the other four metals(6,7,8,9). In the case of nickel at Galt, the effluent values were influenced by a short-term peak in the influent during the sampling period resulting in an extended washout period for the metal.

The magnitude of the mean concentrations of metals in the influent appeared to follow the same order, regardless of the nature of the industrial input. The observed order, from highest to lowest, was: zinc, copper, chromium, nickel, lead and cadmium. Approximately the same concentration of a metal was observed at Waterloo, which received the lowest industrial contribution, as was observed at Galt, which received the highest industrial contribution (Table 5). Metal concentration data for Welland were lower than for the other STPs, an indication of the dilute nature of the influent. The corresponding effluent metal concentration data did not exhibit exactly the same ordered behavior although the trend was the same for the metals occurring at the highest (zinc) and at the lowest (lead and cadmium) mean concentrations.

Table 5
GEOMETRIC MEAN METAL CONCENTRATIONS OBSERVED DURING VARIABILITY STUDY

| | Geometric Mean (µg/L) | | | | | |
|---|---|---|---|---|---|---|
| | Zn | Cu | Cr | Ni | Pb | Cd |
| **Influent** | | | | | | |
| Waterloo | 135 | 110 | 47 | 26 | 14 | 4 |
| Galt | 172 | 125 | 56 | 40 | 11 | 3 |
| Welland | 65 | 31 | 15 | 14 | 8 | 3 |
| **Effluent** | | | | | | |
| Waterloo | 75 | 13 | 27 | 24 | 6 | 4 |
| Galt | 77 | 47 | 30 | 48 | 5 | 2 |
| Welland | 22 | 16 | 9 | 13 | 5 | 2 |

As in the case of metal trace contaminants, Galt showed the highest influent variability in aromatic volatile trace contaminants (Table 3). Although mean values of these volatile trace contaminants in the influent were an order of magnitude lower than for the metal trace contaminants, the variability was considerably higher, particularly for toluene, p,m-xylene, o-xylene and ethyl benzene, and similar to values reported in the literature[(2)]. In most cases, effluent variability was lower than influent variability in terms of RSD values. Except for p,m-xylene and o-xylene for which there are few reported data, the influent mean concentrations of total phenolics and aromatic volatile trace contaminants were much lower than reported in the literature[(10)]. For the most part, the concentrations of the total phenolics and the aromatic volatile trace contaminants were reduced to values near to or at detection limits by secondary treatment. Because no air samples were taken, it cannot be verified whether removal can be attributed to degradation or stripping. Geometric mean values for influents and effluents were nearly always lower than corresponding arithmetic mean values.

The aromatic volatile trace contaminants in the influents demonstrated a trend similar to the metal trace contaminants in order of relative mean concentration values at Waterloo and Galt (Table 6), indicating an apparent independence of industrial wastewater contribution. The observed order of aromatic volatile trace contaminants, from the highest to lowest, was: p,m-xylene, toluene, o-xylene, ethylbenzene and benzene. Welland data were not included in this comparison in view of the low number of aromatic trace volatiles found in the Welland wastewater. No trend was observed for the effluent aromatic volatile trace contaminants probably because all effluent data were very near to detection limits, a level at which it is difficult to discern any significant differences.

Table 6
GEOMETRIC MEAN AROMATIC VOLATILE TRACE ORGANIC CONCENTRATIONS OBSERVED DURING VARIABILITY STUDY

| | Geometric Mean (µg/L) | | | | |
|---|---|---|---|---|---|
| | p,m-Xylene | Toluene | o-Xylene | Ethylbenzene | Benzene |
| **Influent** | | | | | |
| Waterloo | 8.3 | 3.4 | 3.2 | 1.4 | 1.4 |
| Galt | 7.5 | 4.1 | 3.2 | 1.5 | 0.7 |

In the case of chlorinated volatile trace contaminants, Waterloo demonstrated the highest influent variability (Table 4) although several volatiles exhibited high variability in the Galt influent due to periodic high concentrations. The mean influent values of the chlorinated volatile trace contaminants were at least an order of magnitude lower than for the metal trace contaminants, although the variability was of the same order. Effluent variability was lower than influent variability in most cases. The influent mean concentrations of the chlorinated volatile organic trace contaminants were much lower than reported in the literature[(10)]. Dichloromethane occurred in almost all samples at all three plants at concentrations similar to those reported in the literature[(2)]. It is used as the extracting solvent in the analytical protocol and can occur as a contaminant in laboratory glassware. Therefore, data for dichloromethane have been omitted from this presentation in view of the uncertainty of its occurrence. The concentrations of the chlorinated volatile trace contaminants in the effluents were reduced to values near to or at detection limits. It was not possible to discern whether this removal was attributable to degradation or stripping because no air samples were taken. Geometric mean values for influents and effluents were nearly always lower than corresponding arithmetic mean values. Unlike the metal or aromatic volatile trace contaminants, there was no consistency in the order of chlorinated volatile trace contaminants based on mean concentrations due, in part, to the low concentrations usually encountered at the three plants.

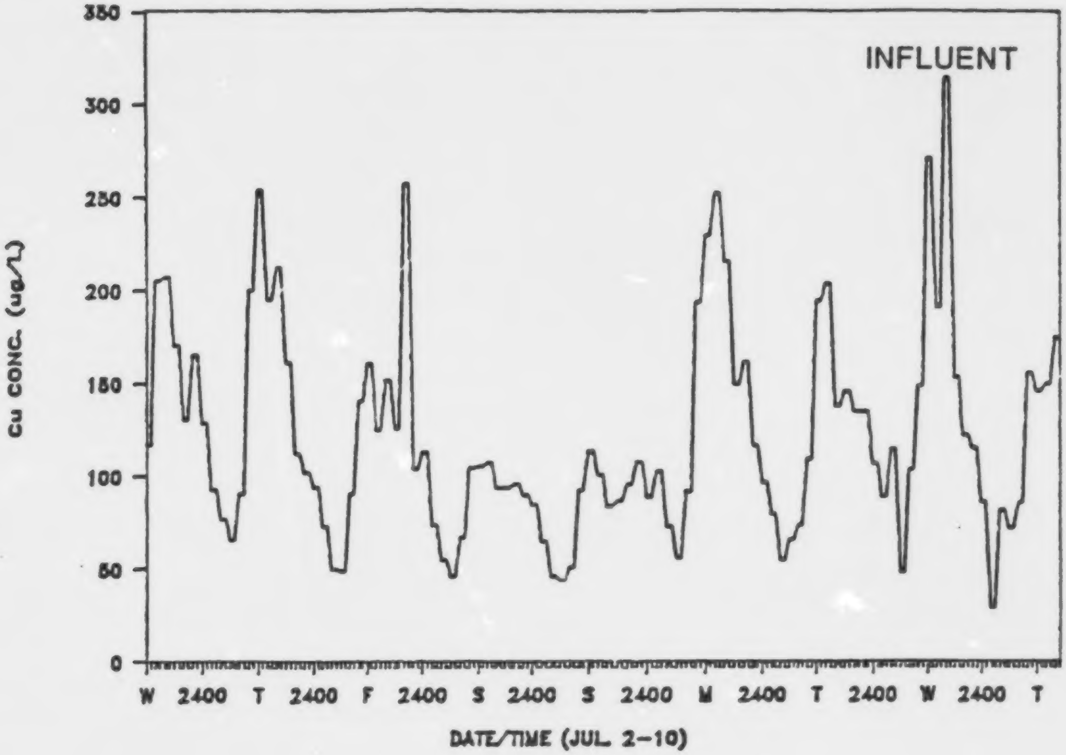
In general, the metal and volatile trace contaminants were more dominant in the influents than the phenolics and PAHs. In secondary effluents, organic trace contaminant concentrations were reduced to values that were usually near to or at the detection limit. Geometric mean values for influents and effluents were always lower than arithmetic mean values. Effluent metal trace contaminant concentrations varied uniquely for each metal at a plant and also between plants.

For the most part, the variability of trace contaminants in the influent, as expressed by the relative standard deviation about the mean, was attenuated in the effluent. The overall variability of trace contaminants in the three treatment plant effluents was not large. This is contrary to the experience reported in the literature where it appears that trace contaminant variability relative to mean concentrations is unchanged by the treatment processes(2). Most information in the literature, however, is based on short-term sampling studies with a small number of data points based on composite samples. This approach may not be appropriate to define the true variability of trace contaminants.

Chronological plots were made of the change in concentration of each trace contaminant during the sampling period. They illustrate a variety of dynamic concentration patterns in influent and effluent streams at each STP. Figures 1 and 2 are examples of such plots for copper and toluene, respectively, in the influent and effluent at the Waterloo STP. Copper concentrations in the influent exhibited a diurnal variation but the effluent concentrations varied randomly. Influent toluene concentrations, on the other hand, varied randomly with periodic peaks. Despite this variability, toluene was removed to detection limits for much of the time.

MISA Thirty-Seven Plant Study. Concentrations of metals, aromatic volatiles and total phenolics, and chlorinated volatiles in raw sewage at all 37 WPCPs included in the MISA pilot monitoring study and in final effluents from the 27 secondary treatment plants are presented in Tables 7, 8 and 9, respectively. It is reiterated that only those compounds which were identified in the variability study (Tables 2, 3 and 4) are presented in Tables 7, 8 and 9. Presented for each compound are the geometric mean concentration and the spread factor.

Concentrations of heavy metals in the larger sample population were generally in agreement with those observed in the three plants sampled intensively during the variability study. The order of metals from highest to lowest in concentration in the raw sewage also agreed in the MISA sampling with that observed in the variability study with the exception of lead, which was found at a higher mean concentration in the 37 WPCPs sampled during the MISA study.



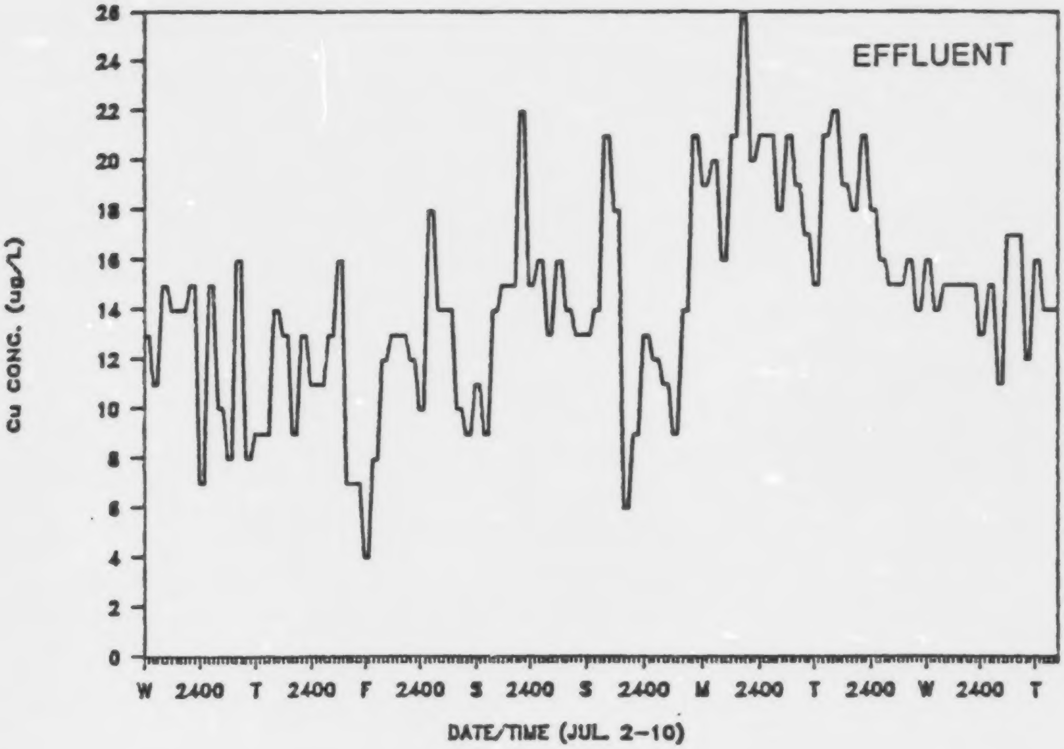


FIGURE 1: CHRONOLOGY OF INFLUENT AND EFFLUENT COPPER AT WATERLOO WPCP

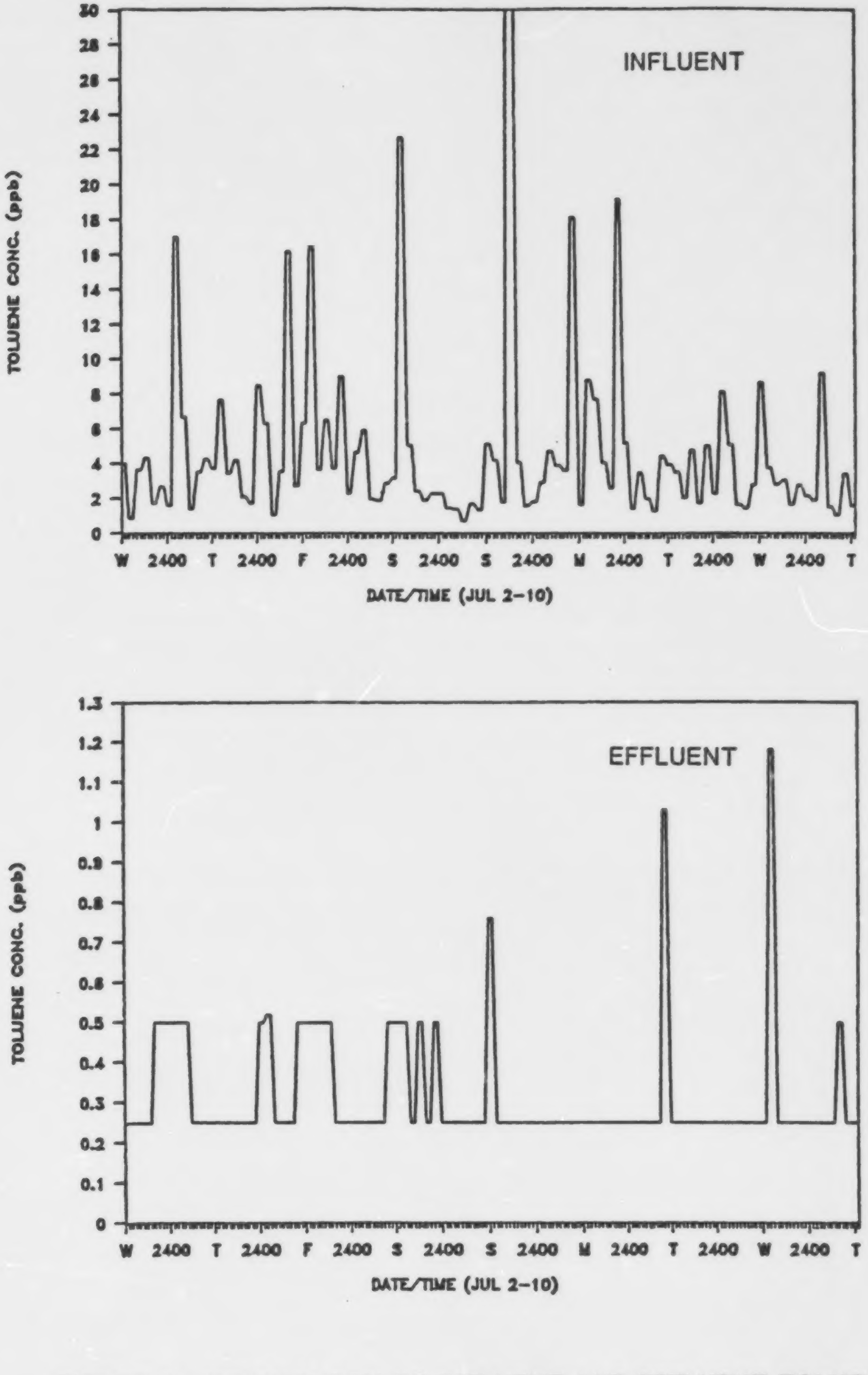


FIGURE 2: CHRONOLOGY OF INFLUENT AND EFFLUENT TOLUENE AT WATERLOO WPCP

## Table 7
## SUMMARY OF METAL CONTAMINANT DATA - MISA PILOT STUDY

| | Cadmium | | Chromium | | Copper | | Nickel | | Lead | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GM[1] | SF[2] | GM | SF | GM | SF | GM | SF | GM | SF | GM | SF |
| Influent | 6.5 | 2.1 | 51.1 | 3.4 | 110.6 | 2.3 | 38.8 | 2.7 | 59.5 | 1.9 | 211.0 | 2.9 |
| Effluent | 2.1 | 2.1 | 9.0 | 2.0 | 13.1 | 2.6 | 22.1 | 3.6 | 16.5 | 1.5 | 53.3 | 2.5 |

---

[1] Geometric mean for influent and effluent in µg/L

[2] Spread factor.

## Table 8
## SUMMARY OF TOTAL PHENOLICS AND AROMATIC VOLATILE TRACE ORGANIC DATA - MISA PILOT STUDY

| | Total Phenolics | | p,m-Xylene | | o-Xylene | | Ethylbenzene | |
|---|---|---|---|---|---|---|---|---|
| | GM[1] | SF[2] | GM | SF | GM | SF | GM | SF |
| Influent | 310 | 2.1 | 26.0 | 2.0 | 22.5 | 1.6 | 23.5 | 1.8 |
| Effluent | 70 | 1.9 | 1.1 | 1.5 | 1.1 | 1.4 | 1.0 | 1.2 |

---

[1] Geometric mean for influent and effluent in µg/L

[2] Spread factor.

## Table 9
## SUMMARY OF CHLORINATED VOLATILE TRACE ORGANIC DATA - MISA PILOT STUDY

| | Chloroform | | Trichloroethylene | | 1,1,1-Trichloroethane | | Tetrachloroethylene | |
|---|---|---|---|---|---|---|---|---|
| | GM[1] | SF[2] | GM | SF | GM | SF | GM | SF |
| Influent | 23.9 | 1.8 | 22.6 | 1.8 | 23.2 | 1.7 | 21.5 | 1.5 |
| Effluent | - | - | 1.1 | 1.6 | 1.9 | 1.9 | 1.2 | 1.9 |

---

[1] Geometric mean for influent and effluent in µg/L

[2] Spread factor.

Based on the flow-proportioned sampling approach used during the MISA sampling program, the spread factors of the influent and effluent metal concentration data suggest that there is a comparable amount of variability in the influent and effluent streams from municipal STPs, contrary to the findings of the variability study, but consistent with other studies based on composite sampling approaches.

Geometric mean influent concentrations of trace organic contaminants reported from the MISA study (Tables 8 and 9) were significantly higher than reported in the variability study. This relates directly to the different analytical protocols used and the different detection limits applied during the studies. In the MISA study, detection limits for volatile organics were generally 40 µg/L. Table 10 indicates the total number of influent samples analyzed and the percentage of samples in which each volatile organic compound was identified at a concentration above the detection limit. The highest frequency of detection was approximately 16 percent, for p,m-xylene. The geometric means reported in Tables 8 and 9 for influent samples were calculated by setting any value below the detection limit (DL) as equal to one-half of the detection limit. Thus, geometric mean volatile organic concentrations reported exceed 20 µg/L (0.5 x DL) in all cases. Benzene and toluene are not reported in Table 8 due to elevated method blank results. 1,4-dichlorobenzene was not detected in raw sewage or secondary effluents at concentrations above the detection limits during the MISA study.

Table 10
FREQUENCY OF DETECTION OF VOLATILE ORGANICS
IN RAW SEWAGE DURING MISA STUDY

| Compound | No. of Samples | Frequency of Detection (%) | Detection Limit (µg/L) |
|---|---|---|---|
| p-, m-Xylene | 274 | 15.7 | 40.0 |
| Ethylbenzene | 274 | 11.0 | 40.0 |
| Chloroform | 274 | 10.2 | 40.0 |
| o-Xylene | 274 | 9.1 | 40.0 |
| 1,1,1-Trichloroethane | 274 | 7.7 | 40.0 |
| Trichloroethylene | 274 | 5.5 | 40.0 |
| Tetrachloroethylene | 274 | 4.4 | 40.0 |

Concentrations of volatile organics in secondary effluents sampled under the MISA program were in closer agreement with those measured during the variability study. In the case of effluents, detection limits were generally 2.0 µg/L in the MISA study. As summarized in Table 11, frequency of detection of the selected volatile organics in secondary effluents was less than 10 percent during the MISA program. Thus, with the convention of applying a value equal to one-half of the detection limit, the reported geometric mean concentration of all volatile species in Tables 8 and 9 exceeds 1.0 µg/L (0.5 x DL).

## Table 11
## FREQUENCY OF DETECTION OF VOLATILE ORGANICS IN SECONDARY EFFLUENTS DURING MISA STUDY

| Compound | No. of Samples | Frequency of Detection (%) | Detection Limit (µg/L) |
|---|---|---|---|
| p-, m-Xylene | 224 | 2.2 | 2.0 |
| Ethylbenzene | 224 | 1.3 | 2.0 |
| o-Xylene | 224 | 2.2 | 2.0 |
| 1,1,1-Trichloroethane | 224 | 8.0 | 2.0 |
| Trichloroethylene | 224 | 7.6 | 2.0 |
| Tetrachloroethylene | 224 | 8.0 | 2.0 |

The order of magnitude differences in detection limits applied to raw sewage and effluents during the MISA program causes difficulties in comparing the variability of influent and effluent streams based on these data. Further, the 'between plant' variability of the trace organic compounds based on the MISA study cannot be compared with the 'in-plant' variability of these compounds based on the results of the variability study.

## CONCLUSIONS

- Metals were the dominant trace contaminants in influents and effluents from the municipal STPs investigated. Of the metals analyzed during both the variability study and the MISA 37 plant study, zinc and copper were present at the highest average concentrations in [illegible]. Cadmium was present at the lowest average concentration.

- Based on the findings of the variability study, the variability of trace contaminants in the influent was attenuated in the effluent.

- Geometric mean values of trace contaminants in influents and effluents were lower than corresponding arithmetic means in most cases. Removals of trace contaminants may be overstated in terms of arithmetic means as compared to removals based on geometric mean values. Trace contaminant data are more appropriately described by a non-normal distribution function and average values as geometric means.

- Reported mean concentration data are influenced by the analytical detection limits applied and the method used to handie non-detected concentration values in the data.

## REFERENCES

1. Richards, D.J. and Shieh, W.K. (1986). "Biological Fate of Organic Pollutants in the Aquatic Environment", Wat. Res., 20, 1077-1090.

2. Monteith, H. (1987). Fluctuations of Trace Contaminants in Sewage Treatment Plants. Monograph Series on Advances in Water Pollution Research & Technology, No. 1. Canadian Association of Water Pollution Control, Burlington, Ontario, Canada.

3. Canviro Consultants (1988). "Thirty-seven Municipal Water Pollution Control Plants PIlot Monitoring Study, Volume I, Interim Report". Report prepared for Ontario Ministry of Environment, Water Resources Branch, Toronto, Ontario, Canada.

4. Melcer, H., Monteith, H. and Nutt, S.G. (1988). "Variability of Toxic Trace Contaminants in Municipal Sewage Treatment Plants". Wat. Sci. Tech., 20, 275-284.

5. Melcer, H. et al (1989). "Dynamic Modelling of Trace Contaminant Removal in a Municipal Sewage Treatment plant". Wat. Sci. Tech., 21, 351-362.

6. Burns and Roe Industrial Services Corporation (1982). "Fate of Priority Toxic Pollutants in Publicly Owned Treatment Works - Final Report, Vol. 1". NTIS Pub. No. EPA-440/1-82/303.

7. Hannah, S.A. and Rossman, L.A. (1982). "Monitoring and Analysis of Hazardous Organics in Municipal Wastewater - A Study of 25 Treatment Plants". NTIS Pub. No. PB83-155713.

8. Lester, J.N. (1983). Significance of Behaviour of Heavy Metals in Wastewater Treatment Processes - I. Sewage Treatment and Effluent Discharge. Sci. of the Tot. Env., 30, 1-44.

9. Nielsen, J.S. and Hrudey, S.E. (1983). Metal Loadings and Removal at a Municipal Activated Sludge Plant. Wat. Res., 17, 1041-1052.

10. Melcer, H. (1986). Control of Toxic Trace Contaminants in Municipal Wastewater Treatment Plants. Proceedings of Ontario Ministry of Environment Technology Transfer Conference, Ontario MOE, Toronto, Ontario, 27-52.

## ACKNOWLEDGEMENTS

Some of the information in this paper was published previously in Water Science and Technology.

## BIOGRAPHICAL DATA

Mr. Nutt is the Manager of the Wastewater Reclamation Division in CH2M HILL ENGINEERING LTD.'s Waterloo, Ontario office. He has been involved as a consultant in the environmental engineering field for 16 years, specializing in the design and optimization of industrial and municipal wastewater treatment facilities. During the last ten years he has been involved on behalf of both public and private sector clients in identifying the sources and fates of trace contaminants in treatment plants and has presented numerous papers on the subject.

# STRIPPING OF VOLATILE ORGANIC COMPOUNDS AT MUNICIPAL WASTEWATER TREATMENT PLANTS

Henryk Melcer
Environment Canada
Wastewater Technology Centre
PO Box 5050, Burlington, Ontario, Canada

Doug Thompson, John Bell
Enviromega Ltd.
PO Box 121
Campbellville, Ontario, Canada

Hugh Monteith
Municipal Section
Ontario Ministry of the Environment
Toronto, Ontario, Canada

The stripping of volatile organic compounds (VOCs) from municipal wastewater treatment plant aeration basins was studied at pilot plant and full scale. The percentage of volatiles stripped from these aeration basins was established both in presence and absence of biomass. Of 37 VOCs examined, the loss of 15 non-chlorinated VOCs was attributed primarily to biological removal. Biological removal was shown to be only a minor removal mechanism for seven chlorinated VOCs. Stripping was the major removal mechanism for the chlorinated VOCs. Adsorption of VOCs on biomass occurred to a very minor extent. Stripping was shown to increase non-linearly with increased air flowrates. These data were used to model the stripping process.

## Introduction

Volatile organic compounds (VOCs) have been reported to occur consistently in municipal wastewater treatment plant influents[1]. These compounds are stripped from wastewater during aeration and are of interest to health and environmental regulatory authorities in Ontario. Work has been aimed at developing theoretical and empirical models to predict stripping of VOCs from wastewater treatment plants[2,3], but these models do not appear to have been conclusively proven in field applications. Accordingly, an investigation was undertaken by Environment Canada's Wastewater Technology Centre for the Ontario Ministry of the Environment (MOE) to measure the release of VOCs to the atmosphere.

In Phase I, conducted in 1987, off-gas sampling was carried out at four Ontario municipal wastewater treatment plants to measure the removal of VOCs by air stripping. Those results have been reported elsewhere[4]. In Phase II, conducted in 1988, both pilot plant and full scale investigations were carried out to validate the sampling and analytical protocols used during Phase I and to examine the fate of the most frequently observed VOCs in an activated sludge aeration basin. This paper reports on the results from Phase II.

## Experimental Methods

### Pilot Plant Description

The pilot plant consisted of a 5m$^3$, 3m high aeration basin with primary and secondary settlers each 1.5m diameter and 2m deep (Figure 1). A Rhodamine dye study revealed that the aeration basin contents were completely mixed at all air flowrates employed during the study. A secondary influent line was provided after the primary settler to allow for continuous injection of VOCs. The aeration basin was equipped with coarse and fine bubble diffused aerators which could be operated independently. The airflow rate to the plant was measured using a rotameter. Influent and return activated sludge flowrates, influent temperature, pH and mixed liquor dissolved oxygen concentration were continuously monitored. Primary settler effluent was fed into an overflow tank and was pumped at a controlled rate into the aeration basin. Sludge was wasted from the system daily into a calibrated tank to measure sludge volume for solids retention time (SRT) control.

### Experimental Approach

Four sets of experiments were conducted. The stripping of VOCs from water, in the absence of biodegradation, was assessed by using tap water dosed with ten candidate VOCs as the pilot plant influent. Compounds representing a broad range of chemical structure that were consistently observed in the influents sampled during Phase I were selected for dosing. Target influent VOC concentrations were selected to represent the typical range of influent VOC concentrations observed during Phase I. The candidate compounds and the target influent concentrations are shown in Table I. For each VOC a mass balance was performed around the aeration basin using the aeration basin influent, secondary settler effluent, waste solids and aeration basin off-gas VOC concentration measurements. The mass balance closure was a measure of the accuracy of the sampling and analytical protocol.

The second set of experiments examined the removal of VOCs in the presence of activated sludge. The plant was operated using a continuous supply of raw, degritted sewage from the Burlington Skyway Wastewater Treatment Plant. The same ten candidate VOCs were dosed into the primary effluent and a mass balance was performed around the aeration basin.

The third set of experiments constituted a control to verify that VOC removals were not inadvertently influenced by using VOC dosing levels beyond that at which the sludge was acclimated. The pilot plant received a continuous supply of non-dosed sewage from the Burlington plant and VOC emissions were measured as described earlier. To obtain sewage containing a higher proportion of industrial wastewaters, the plant was moved to Scarborough, Ontario and operated using primary effluent from the Highland Creek Wastewater Treatment Plant.

In the fourth set of experiments, the pilot plant was operated in parallel with a Highland Creek Plant aeration basin. The pilot plant received non-dosed sewage. VOC emissions were measured simultaneously from the pilot plant and the field aeration basin to determine how closely the pilot plant represented field stripping conditions.

## Experimental Protocol

For the dosed tap water and wastewater experiments, the dosing solution was continuously injected into the primary effluent for 26 hours which represented approximately 4 hydraulic residence times (HRTs) of the pilot plant aeration basin and secondary settler. The aeration basin off-gas was continuously sampled between the 25th and 26th hour of dosing. Liquid samples were taken from the influent to the aeration basin and the secondary clarifier effluent at the beginning and end of the off-gas sampling interval. The air flow rate to the plant was constant throughout the dosing period. For the non-dosed wastewater experiments, the pilot plant aeration basin off-gas was sampled continuously for three hours and aeration basin influent and secondary clarifier effluent samples were taken at one hour intervals.

For the final set of experiments, the pilot plant primary settler was not employed, but a pump submerged approximately 0.5m in a Highland Creek primary settler supplied the pilot plant with primary effluent. Thus, the pilot plant and the field aeration basin received essentially the same primary effluent. Field off-gas sampling chambers were located at the influent end, centre and effluent end of the field aeration basin. Off-gas samples were taken for one hour simultaneously from the pilot plant aeration basin vent stack and from the three field off-gas sampling locations. Liquid samples were taken from 6 locations at the beginning and end of the off-gas sampling interval: pilot plant influent and effluent, field aeration basin influent and the three field off-gas sampling locations. Further details on these procedures are published elsewhere[5].

## Conventional Operating Parameters

Mean values of the pilot plant conventional operating parameters are summarized in Table II. $BOD_5$ treatment efficiency exceeded 90% at the Burlington Skyway and Highland Creek sites. Airflow rate was varied for experimental purposes, but ranged between 0.04 and 0.16 $m^3/m^3\cdot min$. The mixed liquor dissolved oxygen concentration was maintained above 1 mg/L at all times. The larger value of MLSS concentration at the Highland Creek site was attributed to the higher organic load.

## Off-gas Sampling and Analysis

The aeration basin and both settlers were covered and vented to the atmosphere. The vent stack above the aeration basin was dampered and the pressure monitored. A slight positive gauge pressure was maintained ( $<$ 2.5 cm water) to ensure that no ambient air leaked into the vent system. Aeration basin off-gas samples were taken from the 10cm diameter vent stack approximately 0.5m above the liquid level of the aeration basin. An off-gas sample was continually drawn from the centre of the vent stack via a 6.4mm diameter stainless steel sample line. The sample stream was passed through a Tenax adsorbent trap where the VOCs were collected. The sample line and adsorbent trap were maintained above 10°C to protect against condensation. The sample stream was drawn though the trap by the vacuum created by pumping water from a closed 5L cylinder with a peristaltic pump. The volume of water pumped from the cylinder was measured at the end of each sampling experiment to determine the volume of gas drawn through the trap. The off-gas sample volume ranged from 0.5L to 4.0L and was adjusted to ensure that the analytical calibration limit was not exceeded.

Field off-gas samples were collected from 1.49$m^2$ floating chambers secured by ropes in the field aeration basins. The off-gas chambers were placed in the field aeration basin for 24 hours before sampling to ensure that they contained a representative off-gas sample. The sampling procedure was very similar to that employed at the pilot plant and a full description is provided by Bell *et al*[6].

The adsorbent traps consisted of stainless steel sampling cartridges packed with 60/80 mesh Tenax GC. The tubes were 175 mm long and 15 mm wide with Swagelock 316 stainless steel end fittings and caps. Tubes were packed with 2.5g of Tenax which was prepared by overnight solvent extraction with methanol, followed by overnight solvent extraction with pentane. The Tenax was dried in a vacuum oven at 120°C for six hours and was sandwiched between plugs of silanized glass wool in the cartridges. The cartridges were conditioned overnight by passing 100mL/min ultra-high purity He through them at 280°C.

The Tenax traps were analyzed for the presence of 37 VOCs on the MOE Effluent Monitoring Priority Pollutant List[4]. Analysis was performed with an automated thermal desorption system (Wang Consultants) interfaced with a Hewlett Packard (HP) 5890 gas chromatograph with an HP mass selective detector (MSD). Cartridges were purged with He at 50cc/min while being heated to 200°C during the desorption stage. Desorption time was 30 minutes. Volatiles were collected on a nickel trap maintained at -195°C with liquid nitrogen and filled with 60/80 mesh inert glass beads to increase trapping efficiency. A Perma Pure dryer (Perma Pure Inc., Farmingdale N.J.) prior to the cold trap removed moisture and polar organics from the sample stream. The trap was flash heated to 150°C delivering collected volatiles on to a 60m DB-1 (0.32mm ID, 1.0 micron film thickness) stationary phase capillary column. Eluents were analyzed by MSD.

The calibration procedure for analysis of volatile organic compounds in off-gas was examined independently during this study. The results of this investigation are presented elsewhere[5]. The external standard calibration method was used. The calibration flask consisted of a 3.0 L spherical glass flask with dual sampling ports. The ports were designed such that teflon stopcocks located in-line between the flask body and septum assemblies maintained the chamber integrity during intervals between sampling. Approximately 10µL of a neat gravimetric standard of target compounds was added to the clean nitrogen filled flask. The flask was sealed and heated to between 150 and 170°C. At least 2.0 hours were allowed for vaporization and mixing of the sample. The flask was then allowed to cool to room temperature and aliquots of the gas were drawn off for calibration. For each target compound, a five level linear calibration plot was constructed. Calibration was rechecked with the neat standard mixture as described on a weekly basis. An instrument performance reference standard of n-alkanes (Supelco, cat. no 2-3444) was run daily. A response deviation of greater than 10% resulted in a full instrument recalibration.

Off-gas analytical quality assurance was monitored using blanks, precision tests, breakthrough tests and recovery tests. Bell _et al_[4] have reported in detail a similar quality assurance monitoring program. Blank traps containing clean Tenax were analyzed in the same manner as described above. For most compounds the blank concentrations were consistently less than 1% of the sample concentrations. However, high concentrations of toluene, and to a much lesser extent dichloromethane, were observed for a period. The source of the high blank level was discovered to be an air leak in the laboratory thermal desorber which was contaminating the Tenax. All toluene off-gas data analyzed during this period were discarded. Approximately 25% of the off-gas samples were measured in duplicate. The coefficients of variation for the duplicate tests were generally less than 20%, indicating good precision for the sampling and analytical methods. Four breakthrough tests were conducted by placing a second trap in series with, and downstream of, the primary trap. However, for all compounds, the concentration of VOCs on the second trap was less than 2% of the sample concentration. Finally, analytical recovery tests indicated recoveries for a large number of VOCs in the range of 80 to 100%.

### Wastewater Sampling and Analysis

Influent wastewater samples were taken from a sample port immediately before the entrance to the aeration basin. Effluent samples were taken from the secondary settler discharge. Wastewater samples were collected in 60mL amber, septum top bottles. The samples were refrigerated at 4°C during storage and transported to the analytical laboratory. Samples were analyzed using purge and trap gas chromatography/mass spectroscopy (modified version of U.S. EPA method 624) within 5 days of collection.

### Dosing Procedure

The dosing compounds were contained in a 35L Tedlar bag filled with 34L of water and 1L methanol. The methanol was used to encourage solubility. A pure methanol solvent was not used because of the possibility of VOC precipitation when mixed with the sewage. A measured quantity of each VOC was injected into the bag to achieve the target influent VOC concentration. The dose solution was pumped through 9.5mm Viton tubing into the sewage line by a calibrated peristaltic pump. As the bag contents were emptied the bag collapsed upon itself and eliminated any headspace. The flowrates of the dose stream and the plant influent stream were measured. A helical static mixer was placed in the plant influent line to ensure total mixing of the VOC solution with the primary settler effluent.

Preparation of the dosing solution was initiated by pumping distilled water into the Tedlar bag through Viton tubing. Measured aliquots of five VOCs were then drawn into a 25 mL syringe partially filled with methanol. 1,4 dichlorobenzene is a solid at room temperature and had to be dissolved in methanol. The syringe then pierced the Viton tubing and the solution was injected into the line as close to the Tedlar bag as possible. The flow of water carried the VOCs into the Tedlar bag. The procedure was then repeated for the remaining five VOCs. Finally, the Tedlar bag was gently stirred for 24 hours using a magnetic stir bar. A number of VOC droplets were visible after filling the bag, but these disappeared after 24 hours of stirring.

## Results

### Mass Balance

For each pilot plant experiment the concentration and mass flowrates of each VOC in the influent, effluent, off-gas and waste activated sludge (WAS) were calculated. The measured concentration of VOCs in the waste activated sludge were more sporadic than the effluent concentrations but not significantly higher. Since the volume of sludge wasted daily to maintain a 5 day SRT is much less than the effluent flow, sorption on the waste activated sludge was not considered a major VOC removal mechanism.

For each VOC the mass balance closure was defined as the total measured off-gas VOC mass flow plus the total measured effluent VOC mass flow and the measured waste sludge VOC mass flow divided by the measured influent VOC mass flow. Table III contains a sample calculation of the mass balance closure.

Table IV summarizes the percentage mass balance closure of the 10 candidate VOCs for the dosed tap water experiments and for the wastewater experiments employing Burlington Skyway and Highland Creek sewages. There was no difference in the observed mass balance closure between the dosed and non-dosed experiments and the results have been combined. Dosed tap water mass balance closures ranged from 68% to 123% indicating reasonable sampling and analytical accuracy. For the wastewater experiments, the mass balance closures for toluene, 4-ethyl toluene, 1,3,5-trimethylbenzene and p-xylene were 11% or less and well below those values observed during dosed tap water experiments suggesting that, in the absence of significant observed adsorption, biological removal appeared to be the dominant removal mechanism for these compounds rather than stripping. The mass balance closures for the remaining 6 candidate compounds ranged from 11% to 104% and were moderately lower than those observed during dosed tap water experiments suggesting a limited amount of biological removal of these VOCs and a dominance of stripping. Mass balance closures were generally lower at the Highland Creek site than at Burlington Skyway suggesting greater biological removal due, possibly, to the higher MLSS concentration at Highland Creek.

Table IV also lists the mass balance closure for 12 VOCs on the MOE Effluent Monitoring Priority Pollutant List[6], other than the candidate ten, observed in the Highland Creek or Burlington Skyway sewages. Mass balance closures for all compounds except 1,1-dichloroethane were consistently below 10% suggesting significant biological removal. The average mass balance closure for 1,1-dichloroethane was 30% suggesting less biological removal. Summing the candidate and non-candidate compounds, the 7 VOCs that exhibited incomplete biological removal were chlorinated and the 15 VOCs that exhibited nearly complete biological removal were non-chlorinated.

## Stripping Model

Matter-Muller et al[7] presented an expression for predicting the relationship between gas-phase VOC concentration and liquid phase VOC concentration in a diffused aeration system. They recognized a limitation in the Henry's law description of saturation in aerated wastewater applications by introducing a fractional saturation term in their relationship. They defined fractional saturation as the ratio of the measured off-gas concentration to the saturation off-gas concentration predicted from Henry's Law. Fractional saturation is predicted by,

$$f = 1-\exp(K_L aV/HQ_G) \quad \text{.......................................(1)}$$

where:

$f$ = fractional saturation,
$K_La$ = stripping mass transfer coefficient ($hr^{-1}$),
$H$ = dimensionless Henry's Law Constant,
$V$ = aeration tank volume ($m^3$), and
$Q_G$ = airflow rate ($m^3/hr$).

In this work, it was recognized that similarity needed to be established between the stripping process in the pilot plant and in a full scale aerated basin. To this end, it is known that stripping mass transfer coefficients can be estimated from oxygen mass transfer coefficients using film theory which states that mass transfer coefficients are directly proportional to diffusion coefficients. This suggests that an increase in oxygen $K_LaV/Q_G$ would increase the ratio of the gas phase to liquid phase concentration of the VOC until the gas bubble is saturated with the VOC. Accordingly, the dimensionless term, oxygen $K_LaV/Q_G$, as defined in equation (1), was used to provide a basis for stripping process similarity between the pilot plant and field aeration basin.

Oxygen mass transfer tests were performed on the pilot plant and in aeration basins at the Burlington Skyway and Highland Creek plants. Because coarse bubble diffusers were used at Burlington Skyway and fine bubble diffusers at Highland Creek, the two plants represented a range of typical field oxygen mass transfer conditions. Pilot plant clean water oxygen mass transfer ($K_La$) determinations were performed using standard procedures[8]. Process water $K_La$ was determined using the off-gas technique outlined by Redmon et al[9]. Table V summarizes the results from the oxygen mass transfer tests. The pilot plant aeration basin was not as deep as the field aeration basins, and when filled with mixed liquor, the pilot plant could not achieve the oxygen $K_LaV/Q_G$ of the Highland Creek basin but could achieve it when filled with tap water. Since dosed tap water experiments were employed, the pilot plant was able to span a typical range of field aeration basin oxygen mass transfer conditions.

Table VI records the observed pilot plant aeration basin off-gas fractional saturation for the candidate compounds for each experimental condition. Observed fractional saturation was calculated as the ratio of the gas phase to liquid phase VOC concentration expressed as a fraction of the Henry's Law coefficient. Results using Burlington Skyway and Highland Creek sewage were combined. Henry's Law coefficients were not available for 4-ethyl toluene and 1,3,5-trimethylbenzene. The mixing regime of the aeration basin was demonstrated to be complete mix. Consequently the clarifier effluent VOC concentration was taken to be the same as that of the aeration basin. Predictions of fractional saturation were made using Equation 1 and are shown in Table VI. Also listed in Table VI are values of the dimensionless Henry's Law coefficient obtained from the literature.

For all compounds in Table VI there was no significant difference in observed fractional saturation between wastewater experiments employing the fine and coarse bubble diffusers and therefore no change with changing oxygen $K_La V/Q_G$. Only two tap water experiments were carried out, one with coarse bubble diffusion and the other with fine pore diffusion. Therefore, it cannot be said that these fractional saturation values are statistically similar to those derived from the wastewater experiments. However, the singleton tap water fractional saturation values fall within the confidence limits of the wastewater values, that is, observed fractional saturation did not change as oxygen $K_La V/Q_G$ varied from 1.1 (wastewater-coarse bubble) to 4.5 (tap water-fine bubble). The constant fractional saturation that was observed over varying oxygen mass transfer conditions implies that equilibrium existed between the gas and liquid phases. This appeared to be anomalous because saturation was demonstrated at observed fractional saturation values of less than unity. The difference between the observed fractional saturation and unity may be attributed to two possible reasons: either the error associated with measuring fractional saturation f was greater than the differences between measured and predicted fractional saturation values, or the values of Henry's Law coefficients obtained from the literature were in error.

In most cases, the model predicted a minor decrease in fractional saturation (Table VI) with decreasing values of pilot plant oxygen transfer efficiency (Table V). (The large predicted decrease in fractional saturation for tetrachloroethylene is attributed to the high value of Henry's Law coefficient reported in the literature.) Therefore, in general, the model predicted equilibrium or near equilibrium between the liquid and gas phases across the typical range of field oxygen mass transfer conditions. However, true off-gas VOC concentration predictions are best made by using the observed value of Henry's Law coefficient which may be calculated from the observed fractional saturation values in Table VI multiplied by the Henry's Law coefficients obtained from the literature.

## Pilot Plant/Field Aeration Basin Comparison

Fractional saturation was measured in the pilot plant and field aeration basin during three parallel pilot plant/Highland Creek aeration basin experiments. Table VII summarizes the results. Mixed liquor and off-gas VOC concentrations were taken at three locations in the field aeration basin to provide 9 field basin data points. Except for the anomaly of dichloromethane, there was no difference in the fractional saturation observed in the pilot plant and the field aeration basin. This suggests that the pilot plant adequately represented field stripping conditions and that the pilot plant and field sampling protocols were equivalent.

For the pilot plant and the field aeration basin, mean percentage removal was defined as:

$$\text{Removal} = [1-(C_e/C_i)] \times 100 \qquad (2)$$

where,

$C_e$ = aeration basin effluent VOC concentration
$C_i$ = aeration basin influent VOC concentration

The mean percentage removal of 5 candidate VOCs for the parallel pilot plant and field aeration basin experiments is shown in Table VIII. For the other 5 candidate VOCs, the effluent concentrations were consistently below the analytical method detection limit. For the 5 compounds shown, removals were quite similar indicating that the pilot plant represented field operating conditions.

## Airflow Rate and Stripping

The fraction of each VOC stripped from the pilot plant aeration basin was defined as the ratio of the measured VOC off-gas mass flow divided by the measured VOC influent mass flow. A sample calculation of percentage stripped is contained in Table III. Pilot plant experiments were performed over a range of air flow rates during all wastewater studies, and the results are summarized in Figure 2. The dashed line represents the average percentage stripped for 8 experiments with air flow rates ranging from 0.1 to 0.16 $m^3/m^3 \cdot min$. The solid line represents the average percentage stripped for 11 experiments with air flow rates ranging from 0.04 to 0.06 $m^3/m^3 \cdot min$. These data have not been corrected for tap water mass balance closures. No distinction was made between the diffuser types because it was established that fractional saturation did not change with diffuser type. Results using Burlington sewage and Highland Creek sewage have been combined. The amount of stripping increased with increasing air flow rate, but the relative increase in percentage stripped was less than the relative increase in airflow rate.

## Conclusions

- In a complete mix, 5 day SRT municipal activated sludge system, the loss of 15 non-chlorinated VOCs was attributed to biological removal mechanisms. Stripping was observed to be a minor removal mechanism for these VOCs.

- Seven chlorinated VOCs were removed from the same system primarily by stripping. Biological removal was not observed to be a significant removal mechanism.

- Adsorption was not observed to be a significant removal mechanism for the chlorinated and non-chlorinated VOCs studies, accounting for approximately one percent of VOC loss in the systems examined.

- The off-gas and liquid phase VOC concentrations were in equilbrium across the range of typical field oxygen mass transfer conditions examined, but the observed saturated gas phase VOC concentrations differed from those predicted using Henry's Law coefficients obtained from the literature.

- Stripping increased with increasing air flow rate, but the relative increase in percentage stripped was less than the relative increase in air flow rate.

# References

1. A.C. Petrasek *et al.*, "Fate of Organic Compounds in Municipal Wastewater Treatment Plants", *J. Wat. Pollut. Control Fed.*, *55*: 1286. (1983).

2. P.V. Roberts *et al.*, "Volatilization of Organic Pollutants in Municipal Wastewater Treatment Plants: Model Studies", EPA-600/2-84-047, U.S. Environmental Protection Agency, Cincinnati, Ohio (1984).

3. E. Namkung and B.E. Rittmann, "Estimating Volatile Organic Compound Emissions From Publicly Owned Treatment Works", *J. Wat. Pollut. Control Fed.*, *59*: 670. (1987).

4. J. Bell *et al.*, "Investigation of Stripping of Volatile Organic Contaminants In Municipal Wastewater Treatment Systems-Phase I", Ontario Ministry of Environment, Toronto, Ontario (1988).

5. D. Thompson *et al.*, "Investigation of Stripping of Volatile Organic Contaminants In Municipal Wastewater Treatment Systems-Phase II", Ontario Ministry of Environment, Toronto, Ontario (In preparation).

6. Ontario Ministry of Environment, "The Effluent Monitoring Priority Pollutants List", Ontario Ministry of Environment, Toronto, Ontario (1988).

7. C. Matter-Muller *et al.*, "Transfer of Volatile Substances From Water To The Atmosphere", *Wat. Res* *15*: 1271. (1981).

8. W.C. Boyle *et al.*, "Development of Standard Procedures for Evaluating Oxygen Transfer Devices", EPA-600/2-83-102, U.S. Environmental Protection Agency, Cincinnati, Ohio (1983).

9. D. Redmon *et al.*, "Oxygen Transfer Efficiency Measurements in Mixed Liquor Using Off-gas Techniques", *J. Wat. Pollut. Control Fed.*, *65*: 1338. (1983).

Table I - Candidate VOCs and Target Influent Concentration (µg/L)

| Non Chlorinated Aromatics | | Chlorinated Aliphatics | |
|---|---|---|---|
| Toluene | 30 | Dichloromethane | 70 |
| p-Xylene | 30 | Chloroform | 25 |
| 4-Ethyl Toluene | 20 | 1,1,1-Trichloroethane | 10 |
| 1,3,5-Trimethylbenzene | 30 | Trichloroethylene | 25 |
| | | Tetrachloroethylene | 5 |
| **Chlorinated Aromatics** | | | |
| 1,4-Dichlorobenzene | 15 | | |

Table II - Pilot Plant Conventional Operating Parameters

| Sewage Source | HRT (hours) | SRT (days) | MLSS Conc. (g/L) | Average BOD, Influent (mg/L) | Average BOD, Effluent (mg/L) |
|---|---|---|---|---|---|
| Burlington Skyway | 5.5 | 5 | 2.0 | 110 | 7 |
| Highland Creek | 5.5 | 5 | 3.2 | 150 | 9 |

Table III- Sample Mass Balance Closure Calculation

Effluent Flowrate=13.5 L/min
Air Flowrate=200 L/min
Estimated waste activated sludge flowrate=0.14 L/min

| | **Influent** | **Effluent** | **Off-gas** | **WAS** |
|---|---|---|---|---|
| | Concentration | | | |
| | (μg/L) | (μg/L) | (ng/L) | (μg/L) |
| Dichloromethane | 70.5 | 3.4 | 349.7 | 2.7 |
| Chloroform | 4.3 | 0.5 | 42.3 | 0.3 |
| 1,1,1-Trichloroethane | 245.5 | 12.4 | 2931.9 | 13.8 |
| Toluene | 172.0 | ND | 163.7 | 0.6 |
| Tetrachloroethylene | 1.1 | 0.06 | 45.9 | 0.1 |
| p-Xylene | 9.6 | 0.12 | 21.4 | ND |
| 1,4-Dichlorobenzene | 5.4 | 0.84 | 162.5 | 0.8 |
| | | Flowrate (μg/L) | | |
| Dichloromethane | 952 | 46 | 70 | 0.4 |
| Chloroform | 58 | 7 | 8 | 0.04 |
| 1,1,1-Trichloroethane | 3314 | 168 | 586 | 1.9 |
| Toluene | 2322 | 0 | 33 | 0.08 |
| Tetrachloroethylene | 15 | 1 | 9 | 0.01 |
| p-Xylene | 130 | 2 | 4 | 0.0 |
| 1,4-Dichlorobenzene | 73 | 11 | 33 | 0.1 |

| | Mass Balance Closure (%) | Influent Stripped (%) |
|---|---|---|
| Dichloromethane | 12.2 | 7.4 |
| Chloroform | 25.9 | 13.8 |
| 1,1,1-Trichloroethane | 22.8 | 17.7 |
| Toluene | 1.4 | 1.4 |
| Tetrachloroethylene | 66.7 | 60.0 |
| p-Xylene | 4.6 | 3.1 |
| 1,4-Dichlorobenzene | 60.4 | 45.2 |

Table IV - Mass Balance Closure Summary

|  | Percentage Mass Balance Closure |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | Dosed Tap Water |  | Burlington Sewage |  | Highland Creek Sewage |  |
|  | Avg | Std Dev | Avg | Std Dev | Avg | Std Dev |
| **Candidate VOCs** |  |  |  |  |  |  |
| Tetrachloroethylene | 123 | 50 | 102 | 55 | 104 | 31 |
| 1,4-Dichlorobenzene | 96 | 20 | 92 | 40 | 78 | 24 |
| Trichloroethylene | 71 | 22 | 70 | 43 | 20 | 9 |
| Chloroform | 76 | 31 | 67 | 31 | 54 | 17 |
| 1,1,1-Trichloroethane | 85 | 35 | 55 | 34 | 41 | 14 |
| Dichloromethane | 103 | 29 | 55 | 31 | 11 | 27 |
| p-Xylene | 74 | 14 | 11 | 9 | 5 | 3 |
| Toluene | 68 | 7 | *-- | -- | 4 | 4 |
| 4-Ethyl Toluene | 76 | 19 | 3 | 2 | 4 | 3 |
| 1,3,5-Trimethylbenzene | 69 | 13 | 4 | 3 | 5 | 5 |
| **Non-Candidate VOCs** |  |  |  |  |  |  |
| Ethyl Benzene | NA | NA | <10 | <10 | <10 | <10 |
| m-Xylene | NA | NA | NA | NA | <10 | <10 |
| o-Xylene | NA | NA | <10 | <10 | <10 | <10 |
| Propyl Benzene | NA | NA | <10 | <10 | <10 | <10 |
| Isopropyl Benzene | NA | NA | NA | NA | <10 | <10 |
| 2-Ethyl Toluene | NA | NA | <10 | <10 | <10 | <10 |
| 3-Ethyl Toluene | NA | NA | NA | NA | <10 | <10 |
| 1,2,3-Trimethylbenzene | NA | NA | <10 | <10 | <10 | <10 |
| 1,2,4-Trimethylbenzene | NA | NA | <10 | <10 | <10 | <10 |
| 1,3-Diethylbenzene | NA | NA | <10 | <10 | <10 | <10 |
| 1,4-Diethylbenzene | NA | NA | <10 | <10 | <10 | <10 |
| 1,1-Dichloroethane | NA | NA | NA | NA | 30 | 25 |

*- data discarded because of high off-gas blank concentration

NA- not applicable; compound not contained in influent

Table V - Summary of Oxygen $K_LaV/Q_G$

| | Pilot Plant | | | | Field Aeration Basins | |
|---|---|---|---|---|---|---|
| | Tap Water | | Process Water | | | |
| | Fine Bubble | Coarse Bubble | Fine Bubble | Coarse Bubble | Highland Creek | Burlington Skyway |
| Oxygen $K_LaV/Q_G$ | 4.5 | 2.2 | 1.6 | 1.1 | 3.5 | 1.4 |

Table VI - Observed Fractional Saturation versus Model Predicted Fractional Saturation Values for Pilot Plant Experiments

| | Henry's Law Coeff. H*** | Tap Water | | Process water | | | |
|---|---|---|---|---|---|---|---|
| | | Fine Bubble | Coarse Bubble | Fine Bubble | | Coarse Bubble | |
| | | | | Avg | Std Dev | Avg | Std Dev |
| | | | | Observed | | | |
| Dichloromethane | 0.13 | 0.4 | 0.5 | 0.8 | 0.4 | 0.9 | 0.5 |
| Chloroform | 0.14 | 0.6 | 0.5 | 0.5 | 0.2 | 0.5 | 0.2 |
| 1,1,1-Trichloroethane | 0.20 | 0.9 | 1.8 | 1.3 | 0.6 | 1.2 | 0.5 |
| Trichloroethylene | 0.38 | 0.7 | 0.5 | 0.6 | 0.4 | 0.7 | 0.2 |
| Toluene | 0.25 | 1.5 | 0.6 | **--- | --- | --- | --- |
| Tetrachloroethylene | 1.19 | 0.5 | 0.6 | 0.5 | 0.3 | 0.4 | 0.2 |
| p-Xylene | 0.22 | *--- | 0.9 | **--- | --- | --- | --- |
| 1,4-Dichlorobenzene | 0.11 | 1.0 | 1.0 | 1.5 | 0.3 | 1.1 | 0.4 |
| | | | | Predicted | | | |
| Dichloromethane | | 1.0 | 1.0 | 1.0 | | 0.98 | |
| Chloroform | | 1.0 | 1.0 | 0.98 | | 0.96 | |
| 1,1,1-Trichloroethane | | 1.0 | 0.98 | 0.94 | | 0.86 | |
| Trichloroethylene | | 0.99 | 0.88 | 0.78 | | 0.65 | |
| Toluene | | 1.0 | 0.95 | 0.89 | | 0.78 | |
| Tetrachloroethylene | | 0.71 | 0.45 | 0.36 | | 0.26 | |
| p-Xylene | | 1.0 | 0.95 | 0.90 | | 0.79 | |
| 1,4-Dichlorobenzene | | 1.0 | 1.0 | 0.99 | | 0.96 | |

* - data discarded because of error in liquid sample analysis

** - effluent concentration was below liquid sample detection limit

***- Henry's Law coefficient is dimensionless.

Table VII - Fractional Saturation, Parallel Pilot Plant/Field Aeration Basin Experiments

| | Fractional Saturation | | | |
|---|---|---|---|---|
| | Pilot Plant | | Field Basin | |
| | Avg. | Std. Dev. | Avg. | Std. Dev. |
| Dichloromethane | 1.0 | 0.2 | 0.6 | 0.1 |
| Chloroform | 0.6 | 0.1 | 0.5 | 0.1 |
| 1,1,1-Trichloroethane | 1.1 | 0.1 | 1.1 | 0.3 |
| Tetrachloroethylene | 0.5 | 0.3 | 0.5 | 0.2 |
| 1,4-Dichlorobenzene | 1.6 | 0.1 | 1.5 | 0.3 |

Table VIII - VOC Removal, Parallel Pilot Plant/Field Aeration Basin Experiments

| | Mean VOC Percent Removal | | | |
|---|---|---|---|---|
| | Pilot Plant | | Field Basin | |
| | Avg | Std Dev | Avg | Std Dev |
| Dichloromethane | 93.9 | 3.2 | 94.8 | 2.2 |
| Chloroform | 81.3 | 3.9 | 81.2 | 3.8 |
| 1,1,1 Trichloroethylene | 93.6 | 1.3 | 90.6 | 1.2 |
| Tetrachloroethylene | 86.1 | 2.4 | 76.0 | 15.3 |
| 1,4 Dichlorobenzene | 81.7 | 1.4 | 74.5 | 1.2 |

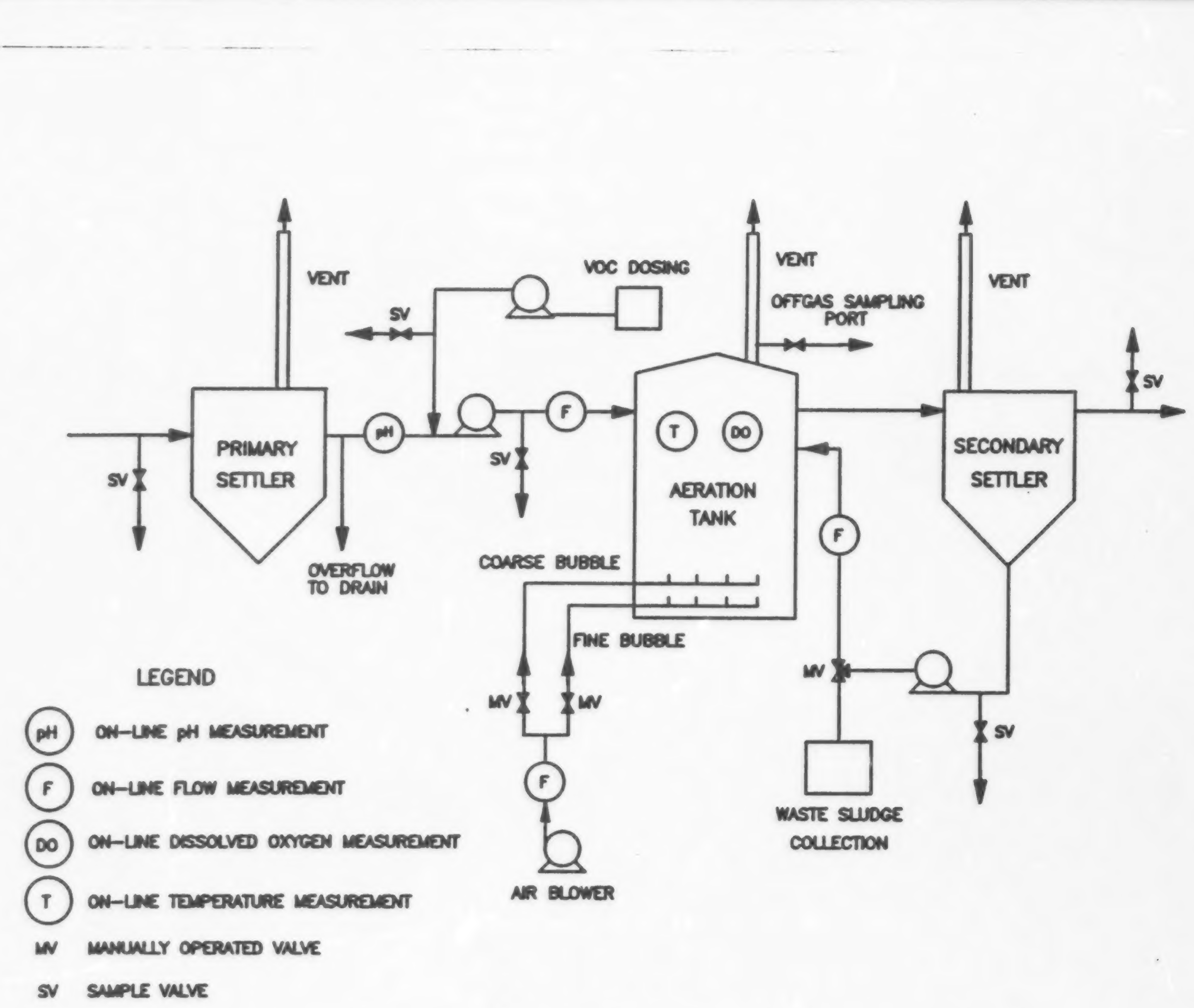

VENT
VOC DOSING
VENT
OFFGAS SAMPLING PORT
VENT
SV
SV
PRIMARY SETTLER
pH
SV
F
T
DO
AERATION TANK
SECONDARY SETTLER
SV
OVERFLOW TO DRAIN
COARSE BUBBLE
F
FINE BUBBLE
MV
MV
MV
F
SV
WASTE SLUDGE COLLECTION
AIR BLOWER
LEGEND
pH ON-LINE pH MEASUREMENT
F ON-LINE FLOW MEASUREMENT
DO ON-LINE DISSOLVED OXYGEN MEASUREMENT
T ON-LINE TEMPERATURE MEASUREMENT
MV MANUALLY OPERATED VALVE
SV SAMPLE VALVE

Figure 1— Pilot Plant Schematic

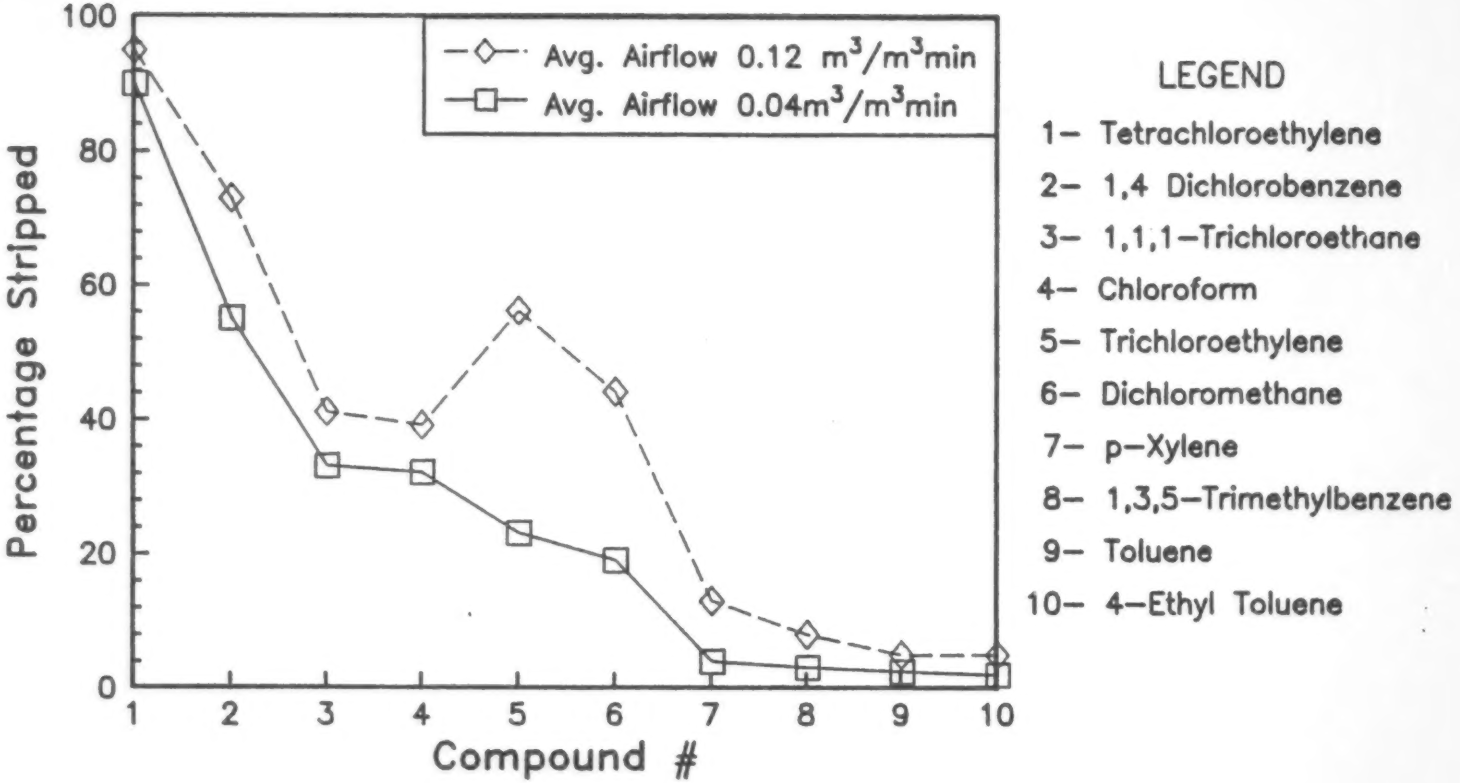


Figure 2– Percentage Stripping and Airflow Rate Summary of Wastewater Experiments

N.B. Data has not been corrected for tap water mass balance closure

Keywords: volatile organic compounds, VOCs, priority pollutants, toxics, stripping, municipal activated sludge treatment plants, adsorption.

# MUNICIPAL SLUDGE, ORGANIC CONTAMINANTS AND AGRICULTURAL UTILIZATION

by

M.D. Webber
Environment Canada
Wastewater Technology Centre

## ABSTRACT

There is concern that organic contaminants in sludge applied to agricultural land may represent health and environmental hazards. Organic contaminant guidelines for sludge use should be developed, however, current information is considered inadequate for this purpose. Measurements of organic contaminants in Canadian sludges were initiated in the early 1980's and a survey of Ontario sludges was conducted in 1987 as part of the Municipal-Industrial Strategy for Abatement (MISA) program. This report presents; (1) a summary of Canadian research and development concerning organic contaminants in municipal sludges and (2) a discussion of organic contaminants in relation to municipal sludge use in agriculture.

## INTRODUCTION

Organic contaminant analysis of waste materials was initiated in Canada during the late 1970's. Environment Canada assumed the lead role and established analytical facilities at the Wastewater Technology Centre (WTC). At first, the focus was on industrial effluents, specifically those from the wood preserving, gold mining and pulp and paper industries. However, interest broadened to include municipal effluents as concern for organic contaminants increased and it was realized that a majority of industries are connected directly to municipal sewer systems. Only large industries in Canada have their own wastewater treatment systems. Results indicated that organic contaminant concentrations in municipal effluents generally were low. Consequently, further analysis was undertaken in the early 1980's to determine whether organic contaminants concentrate in sludge. These early analyses were conducted according to US EPA Priority Pollutant protocols for effluents (Federal Register 1979) and sludges (Warner et al. 1980).

Recently, Ontario has undertaken a Municipal-Industrial Strategy for Abatement program (MISA 1986). Its ultimate goal is the virtual elimination of toxic contaminants in industrial and municipal discharges into waterways. It involves large numbers of effluent and sludge analyses and has generated greatly increased analytical activity in both the public and private sectors.

The focus of this report is organic contaminants in Canadian municipal sludges. It presents: (1) a summary of Canadian research and development in this area and (2) a discussion of organic contaminants in relation to municipal sludge use in agriculture.

## CANADIAN RESEARCH AND DEVELOPMENT CONCERNING ORGANIC CONTAMINANTS IN MUNICIPAL SLUDGE

### Analytical

Initial organic contaminant analyses of municipal sludges conducted at the WTC according to the Warner et al. (1980), protocol were highly variable. It was thought that improvements might be made in this procedure and a study to assess the effects of different extraction techniques on recoveries of base-neutral and acid priority pollutants was conducted (Webber and Lesage 1989). Sixteen compounds chosen to represent different classes of these pollutants were spiked into anaerobically digested sludge and then extracted according to six different methods involving one or more of air drying, dilution, centrifugation, Soxhlet extraction and high speed mixing with a Waring$^R$ blender, ultrasonic probe or Polytron$^R$ mixer. Purgeable pollutants were not included in the study because it was assumed that they would not persist in sludge.

Recoveries varied widely among the pollutants and extraction methods and none of the methods proved ideal. Methods involving air drying, all resulted in losses of the more volatile compounds such as 1,2-dichlorobenzene, nitrobenzene and phenol. Methods involving high speed mixing with the Waring$^R$ blender, ultrasonic probe or Polytron$^R$ mixer were equivalent and the most satisfactory, however, even they exhibited major limitations. For example, results with the Polytron$^R$ mixer (Table 1) indicated that there was no recovery of two compounds, <30% recovery of one compound, <50% recovery of four compounds and much >100% recovery of two compounds. Thus, recoveries which might be considered satisfactory were obtained for only eight to eleven of the sixteen compounds added. The Waring$^R$ blender method required more sample transfers and was more time consuming than the ultrasonic probe and Polytron$^R$ mixer methods.

These results were consistent with US Environmental Protection Agency (US EPA) findings (Haile and Lopez-Avila 1984) and it was concluded that, despite their limitations, sludge extraction methods involving either the ultrasonic probe or Polytron$^{R}$ mixer represented the best available technology. They were adopted for subsequent sludge analyses conducted at the WTC.

**TABLE 1. RECOVERIES OF ORGANIC CONTAMINANTS ADDED TO BURLINGTON ANAEROBICALLY DIGESTED MUNICIPAL SLUDGE**

| Compound | Additions (mg $L^{-1}$) | Recoveries % |
|---|---|---|
| Acenaphthylene | 2 | 90 +/- 6 |
| Benzo(a)pyrene | 2 | 95 +/- 26 |
| Fluoranthene | 2 | 110 +/- 39 |
| 1,2-Dichlorobenzene | 2 | 80 +/- 8 |
| Hexachlorobenzene | 2 | 80 +/- 8 |
| Butyl benzylphthalate | 2 | 156 +/- 13 |
| Bis(2-ethylhexyl)phthalate | 2 | 243 +/- 97 |
| Bis(2-chloroethyl)ether | 2 | 87 +/- 1 |
| 4-Chlorophenyl phenyl ether | 2 | 99 +/- 6 |
| 2,6-Dinitrotoluene | 2 | |
| Hexachloroethane | 2 | |
| Nitrobenzene | 2 | 38 +/- 29 |
| 2,4-Dichlorophenol | 4 | 37 +/- 7 |
| 2,4-Dimethylphenol | 4 | 10 +/- 2 |
| Pentachlorophenol | 12 | 48 +/- 18 |
| Phenol | 6 | 31 +/- 5 |

[a] Average recoveries of 3 replicate analyses +/- relative standard deviations.
Blank space: Compound not detected.

## Organic Contaminants in Canadian Municipal Sludges

During 1980 to 1985, which included the period when the analytical study described above was conducted, samples of Canadian municipal sludges from Vancouver in the west to Halifax in the east were forwarded to the WTC for organic contaminant analysis. They did not result from an organized sludge monitoring study, but were received from wastewater treatment authorities accompanied by requests for information. Some of the sludges were sampled and analyzed several times and others only once. Many of the samples were grabs and represented a single point in time, however, some were composites taken over a period of several days.

Samples of fifteen municipal sludges were analyzed for the EPA base-neutral and acid priority pollutants (Webber and Lesage 1989). Thirteen of the sludges were from industrial centres and were thought to represent worst-case situations for organic contamination. However, analyses indicated that most of the pollutants occurred at low to very low concentrations and in fewer than half of the sludges (Table 2). Analysis was conducted for a total of 55 compounds and of these, 5 compounds; 1,2,3-trichlorobenzene, 3,3'-dichlorobenzidene, hexachlorobutadiene, hexachloropentadiene and 2,4-dinitrophenol were never detected. Fifty occurred at concentrations greater than or equal to the detection limit, 30 occurred at concentrations >1mg kg$^{-1}$ dw and only 10 occurred at concentrations >10 ,mg kg$^{-1}$ dw. The compounds occurring at >10 mg kg$^{-1}$ were mainly phthalate esters observed in all sludges and PAH's observed in one sludge. The elevated concentrations of phthalate esters are thought to result from synthetic polymer industries and plastic piping both of which are widely distributed in large urban communities and the elevated concentrations of PAH's in one sludge were attributed to coking and foundry industries in that sewerage district.

During 1987 an organized sludge monitoring study was conducted as part of Ontario's Municipal-Industrial Strategy for Abatement program (MISA). Five-day composite samples of 34 municipal sludges were collected and analyzed for 144 organic contaminants which included 42 volatile compounds, 57 base-neutral and acid extractable compounds, 35 pesticides and herbicides and 10 dioxin/furan (PCDD/PCDF) compounds. Details of the analytical methods and of QA/QC (quality assurance/quality control) procedures are presented in MISA (1988). Results were reported for both raw and stabilized sludges, however, those for raw sludges are not discussed here because raw sludges may not be utilized on agricultural land in Canada.

Sixty-four organic contaminants were detected in the Ontario stabilized municipal sludges (Table 2). Of these the most prevalent compounds were pesticides and PCB's (polychlorinated biphenyls), with 10 detected at more than 40% of the plants. However, concentrations were low. The highest concentration observed was 2793 μg kg$^{-1}$ dw of 2,4-dichlorophenoxyacetic acid and the highest geometric mean concentration was 114 μg kg$^{-1}$ dw of total PCB's. One dioxin compound (octachlorodibenzodioxin) was detected at 65 per cent of the plants. Its maximum concentration was 304 μg kg$^{-1}$ dw and the geometric mean concentration was 7.1 μg kg$^{-1}$ dw. Tetrachlorodibenzodioxin was not detected in any of the sludges. The most prevalent volatile and base-neutral and acid extractable compounds were detected at 35 per cent of the plants.

Table 2. Organic contaminants in municipal sludges.

| | 15 Canadian Sludges | | | 34 Ontario Stabilized Sludges (MISA Survey) | | |
|---|---|---|---|---|---|---|
| | Occurrence | Concentration (mg/kg dw) | | Occurrence | Concentration (mg/kg dw) | |
| Compound | % | Range | Median | % | Range[c] | Geo. Mean[c] |
| BASE NEUTRAL GROUP: | | | | | | |
| POLYNUCLEAR AROMATICS | | | | | | |
| Acenaphthene | 33 | t[a]-<3 | t | | | |
| Acenaphthylene | 27 | t-5 | t | 2.9 | 6.1 | 1.9 |
| Anthracene | 20 | t-32 | 1 | 2.9 | 4.0 | 1.3 |
| Phenanthrene | 53 | t-36 | 2 | 26.5 | 2.9-28 | 2.2 |
| Benzo(a)anthracene | 7 | <0.5 | | 5.9 | 6.7-15 | 1.4 |
| Chrysene | 27 | t-23 | 1.5 | 11.8 | 9.7-14 | 1.5 |
| Benzo(b)fluoranthene | 7 | <0.5 | | | | |
| Benzo(k)fluoranthene | 13 | <0.5-9 | 5 | 2.9 | 20 | 1.3 |
| Benzo(ghi)perylene | 13 | t-0.3 | 0.2 | | | |
| Benzo(a)pyrene | 13 | 4-7.2 | 5.6 | 2.9 | 11 | 1.3 |
| Dibenzo(ah)anthracene | 7 | <13 | | | | |
| Fluoranthene | 53 | t-33 | 2 | 8.8 | 8.0-22 | 1.3 |
| Fluorene | 60 | t-3 | 2 | 8.8 | 2.6-4.9 | 1.3 |
| Indenol(1,2,3-cd)pyrene | 7 | 7 | | | | |
| Naphthalene | 60 | t-5.8 | 1 | 14.7 | 2.4-26 | 1.5 |
| Pyrene | 67 | t-29 | 3.5 | 8.8 | 9.2-19 | 2.1 |
| CHLORINATED BENZENES | | | | | | |
| 1,2-Dichlorobenzene | 27 | t-1.6 | 0.5 | | | |
| 1,3-Dichlorobenzene | | | | | | |
| 1,4-Dichlorobenzene | 33 | t-1.5[b] | 0.3 | | | |
| Hexachlorobenzene | 7 | 4 | | | | |
| NITROSAMINES | | | | | | |
| N-nitrosodiphenylamine | 27 | t-43 | 16 | 2.9 | 12 | 1.3 |
| N-nitrosodipropylamine | 13 | 2 | 2 | 2.9 | 17 | 1.3 |
| PHTHALATE ESTERS | | | | | | |
| Butyl benzylphthalate | 27 | t-5.7 | 2.5 | 17.7 | 1.7-914 | 1.9 |
| Di-n-butylphthalate | 80 | 0.2-430 | 10 | | | |
| Diethylphthalate | 40 | t-14 | 2.5 | | | |
| Dimethylphthalate | 27 | t-2 | t | | | |
| Di-n-octylphthalate | 60 | t-115 | 7 | | | |
| Bis(2-ethylhexyl)phthalate | 93 | 3-215 | 80 | | | |
| HALOETHERS | | | | | | |
| 4-Bromophenyl phenyl ether | 7 | t | | | | |
| Bis(2-chloroethoxy)methane | 20 | t-0.2 | t | | | |
| Bis(2-chloroethyl)ether | 27 | t-0.3 | 0.1 | | | |
| Bis(2-chloroisopropyl)ether | 13 | t-1 | 0.5 | | | |
| 4-Chlorophenyl phenyl ether | 20 | t-1 | t | | | |
| Diphenylether | | | | 5.9 | 15-30 | 3.2 |
| OTHER COMPOUNDS | | | | | | |
| 2-Chloronaphthalene | 7 | t | | | | |
| 2,4-Dinitrotoluene | 27 | t | t | | | |
| 2,6-Dinitrotoluene | 20 | t-4 | 2 | | | |
| 1,2-Diphenylhydrazine | 13 | t | t | | | |
| Hexachloroethane | 7 | t | | | | |
| Isophorone | 33 | t-71 | 1 | | | |
| Nitrobenzene | 27 | t-9 | 3.5 | 8.8 | 6.4-17 | 1.4 |
| Biphenyl | | | | 2.9 | 6.2 | 1.9 |
| ACID-GROUP: | | | | | | |
| m-cresol | | | | 35.3 | 7.7-2212 | 5.3 |
| p-Chloro-m-cresol | 7 | 0.8 | | | | |
| 2-Chlorophenol | 7 | t | | | | |
| 2,4-Dichlorophenol | 13 | t | | | | |
| 2,4-Dimethylphenol | 13 | t | | | | |
| 4,6-Dinitro-o-cresol | 13 | 1.2-1.5 | 1.3 | | | |
| 2-Nitrophenol | 7 | 1.3 | | | | |
| 4-Nitrophenol | 7 | t | | | | |
| Pentachlorophenol | 7 | t | | | | |
| Phenol | 33 | t-68 | 0.4 | 8.8 | 16-31 | 2.1 |
| 2,4,6-trichlorophenol | 7 | t | | | | |

Table 2. ........ continued

|  | 34 Ontario Stabilized Sludges (MISA Survey) |  |  |
|---|---|---|---|
|  | Occurrence % | Concentration (mg/kg dw) |  |
| Compound |  | Range[c] | Geo. Mean[d] |
| VOLATILES |  |  |  |
| m-,and p-Xylenes | 32.4 | 0.62-1417 | 0.82 |
| Ethylbenzene | 32.4 | 0.18-500 | 0.61 |
| o-Xylene | 32.4 | 0.27-37 | 0.52 |
| Chloroform | 35.3 | 0.008-13 | 0.44 |
| Tetrachloroethylene | 5.9 | 2.8-3.4 | 0.28 |
| 1,4-Dichlorobenzene | 5.9 | 0.22-2.6 | 0.27 |
| Hexanol | 2.9 | 144 | 12 |
| 1,1,1-Trichloroethane | 2.9 | 2.3 | 0.25 |
| Chlorodibromoethane | 2.9 | 6.6 | 0.26 |
| Trichloroethylene | 2.9 | 0.94 | 0.26 |
| DIOXINS AND FURANS |  | (ug/kg dw) |  |
| Octachlorodibenzodioxin | 64.7 | 0.6-304 | 7.1 |
| Heptachlorodibenzodioxin | 23.5 | 1.4-73 | 5.0 |
| Hexachlorodibenzodioxin | 5.9 | 1.1-3.8 | 2.4 |
| Pentachlorodibenzodioxin | 2.9 | 1.3 | 3.2 |
| Pentachlorodibenzofuran | 2.9 | 1.6 | 2.5 |
| PESTICIDES,HERBICIDES,PCBS |  |  |  |
| PP-DDE | 73.5 | 3.6-165 | 11 |
| PCB-total | 67.7 | 34-5592 | 114 |
| 2,4-Dichlorophenoxyacetic acid | 64.7 | 11-2793 | 75 |
| alpha-Chlordane | 55.9 | 4.2-36 | 6.5 |
| 1,2,4-Trichlorobenzene | 52.9 | 13-785 | 15 |
| gamma-Chlordane | 52.9 | 4.9-38 | 6.8 |
| Hexachlorobenzene | 55.9 | 1.1-124 | 7.0 |
| beta-BHC(Hexachlorocyclohexane) | 47.1 | 3.2-622 | 8.8 |
| Silvex | 44.1 | 17-1265 | 93 |
| 2,4,5-Trichlorphenoxyacetic acid | 41.2 | 28-1443 | 84 |
| Dieldrin | 38.2 | 5.8-384 | 6.5 |
| Methoxychlor | 38.2 | 21-7634 | 34 |
| gamma-BHC(Hexachlorocyclohexane) | 35.3 | 5.0-107 | 5.7 |
| Aldrin | 26.5 | 9.6-78 | 5.3 |
| alpha-BHC(Hexachlorocyclohexane) | 32.4 | 4.2-78 | 5.6 |
| Heptachlorepoxide | 23.5 | 4.9-243 | 5.2 |
| Heptachlor | 23.5 | 6.8-28 | 4.7 |
| Mirex | 17.7 | 7.9-81 | 4.9 |
| Hexachlorocyclopentadiene | 23.5 | 28-640 | 34 |
| Endosulfan II | 20.6 | 12-81 | 4.7 |
| PP-DDD | 20.6 | 8.1-68 | 4.6 |
| Endosulfan I | 11.8 | 12-114 | 4.9 |
| Endosulfan sulphate | 17.7 | 35-363 | 18 |
| Oxychlordane | 17.7 | 8.1-27 | 4.2 |
| Endrin | 14.7 | 4.7-57 | 4.2 |
| PP-DDT | 14.7 | 24-182 | 17 |
| PCNB | 14.7 | 60-63 | 23 |
| delta-BHC(Hexachlorocyclohexane) | 11.8 | 2.5-12 | 3.9 |
| Mirex photo | 5.9 | 16-85 | 3.9 |
| Hexachloroethane | 2.9 | 12 | 3.7 |

---

[a] Compound detected but not quantified.
[b] Values are sum of 1,3-dichlorobenzene and 1,4-dichlorobenzene.
[c] Single values indicate only one measurement above detection limit.
[d] Geometric mean includes value of one-half detection limit for non-detects.

The maximum concentrations reported for some compounds in both groups were very high. For example, 1417, 500 and 144 mg kg$^{-1}$ dw, respectively, were reported for m- and p- xylenes, ethylbenzene and hexanol in the volatiles group. Similarly, 2212 and 914 mg kg$^{-1}$ dw, respectively, were reported for m-cresol and butylbenzylphthalate in the base-neutral and acid extractables group. However, the highest geometric mean concentration for volatiles was 12 mg kg$^{-1}$ dw of hexanol, all others were <1 mg kg$^{-1}$ dw, and the highest geometric mean concentration for base-neutral and acid extractables was 5.3 mg kg$^{-1}$ dw for m-cresol.

A comparison of results (Table 2) for the Canadian and Ontario sludges indicated many similarities. For example, individual organic contaminants were seldom observed in more than 50% of the sludges in either group. Contaminant concentrations generally were low and the median data for the Canadian sludges were similar to the geometric mean data for Ontario sludges. Occasional large concentrations, e.g., 2212 mg kg$^{-1}$ dw of m-cresol in an Ontario sludge, were assumed to indicate site-specific contamination problems. Bis(2-ethylhexyl)phthalate concentrations were not reported for the Ontario sludges because QA/QC procedures indicated serious problems with the measurement of this compound.

## Fate of Organic Contaminants in Municipal Sludge Utilized on Agricultural Land

Utilization on agricultural land is a cost-effective method of sludge disposal that recycles essential nutrients to the soil. It is practised widely in Europe and North America and accounts for approximately one-third of Canadian municipal sludge production. Guidelines for sludge use have been developed to minimize health and environmental hazards associated with heavy metals, pathogens and nutrients. However, with the exception of the United States where a PCB limit of 10 mg kg$^{-1}$ dw has been defined for sludge applied to the surface of land for fruit and vegetable production (EPA/FDA/USDA 1981) and 50 mg kg$^{-1}$ dw for sludge applied to other agricultural land (Taylor 1984), the author is not aware of organic contaminant guidelines for sludge use.

There is concern that organic contaminants in municipal sludge applied to agricultural land represent health and environmental hazards. Moreover, there is general agreement that guidelines to minimize these hazards should be developed. However, current information is thought to be inadequate for this purpose and considerable research activity is directed toward obtaining additional information. One such program, sponsored jointly by Environment Canada and the province of Ontario through MISA, is in progress at the WTC. Its objective is to determine the fate of organic contaminants in sludge treated soils. A summary of the results to date follows.

## Volatile Contaminants

Laboratory incubation studies at 22+/-2 °C with four volatile compounds: 1,1-dichloroethane, trichloroethylene, toluene and ethylbenzene each at concentrations of 50 mg $kg^{-1}$ dw indicated that they volatilize and escape rapidly from sludge treated soil (Figure 1). The maximum recoveries of 1,1-dichloroethane and trichloroethylene were attained within 48 hours while for toluene and ethylbenzene, 6 days were required. Total recoveries remained constant throughout the study indicating that there was no significant biodegradation of the compounds. Whereas results indicated 100% recoveries of toluene and ethylbenzene, they indicated only about 60% recoveries of 1,1-dichloroethane and trichloroethylene. A subsequent identical study with 14C-labelled trichloroethylene indicated consistent 100% recoveries of 14C within 48 hours. The discrepancy between recoveries of trichloroethylene by the gas chromatographic and radiotracer techniques remains to be resolved.

## Semi-volatile Compounds

A preliminary laboratory incubation study at room temperature with four semi-volatile compounds: two base-neutral extractables; 1,2,4-trichlorobenzene and chrysene and two acid extractables; phenol and pentachlorophenol each at concentrations of 50 mg $kg^{-1}$ dw, indicated large variations in their persistence in sludge treated soil. Phenol and 1,2,4-trichlorobenzene disappeared completely within a few days whereas pentachlorophenol disappeared slowly after about 40 days and there was no disappearance of chrysene within 200 days. Approximately half the pentachlorophenol disappeared within 200 days, however, both the pentachlorophenol and chrysene data were highly variable indicating analytical difficulties and a need for further study. Initially it was assumed that disappearance of the compounds resulted from biodegradation but a subsequent greenhouse study involving 14C-labelled 1,2,4-trichlorobenzene indicated loss from volatilization. Thus, it is probable that the losses of 1,2,4-trichlorobenzene and phenol, which have similar vapour pressures, resulted from both biodegradation and volatilization.

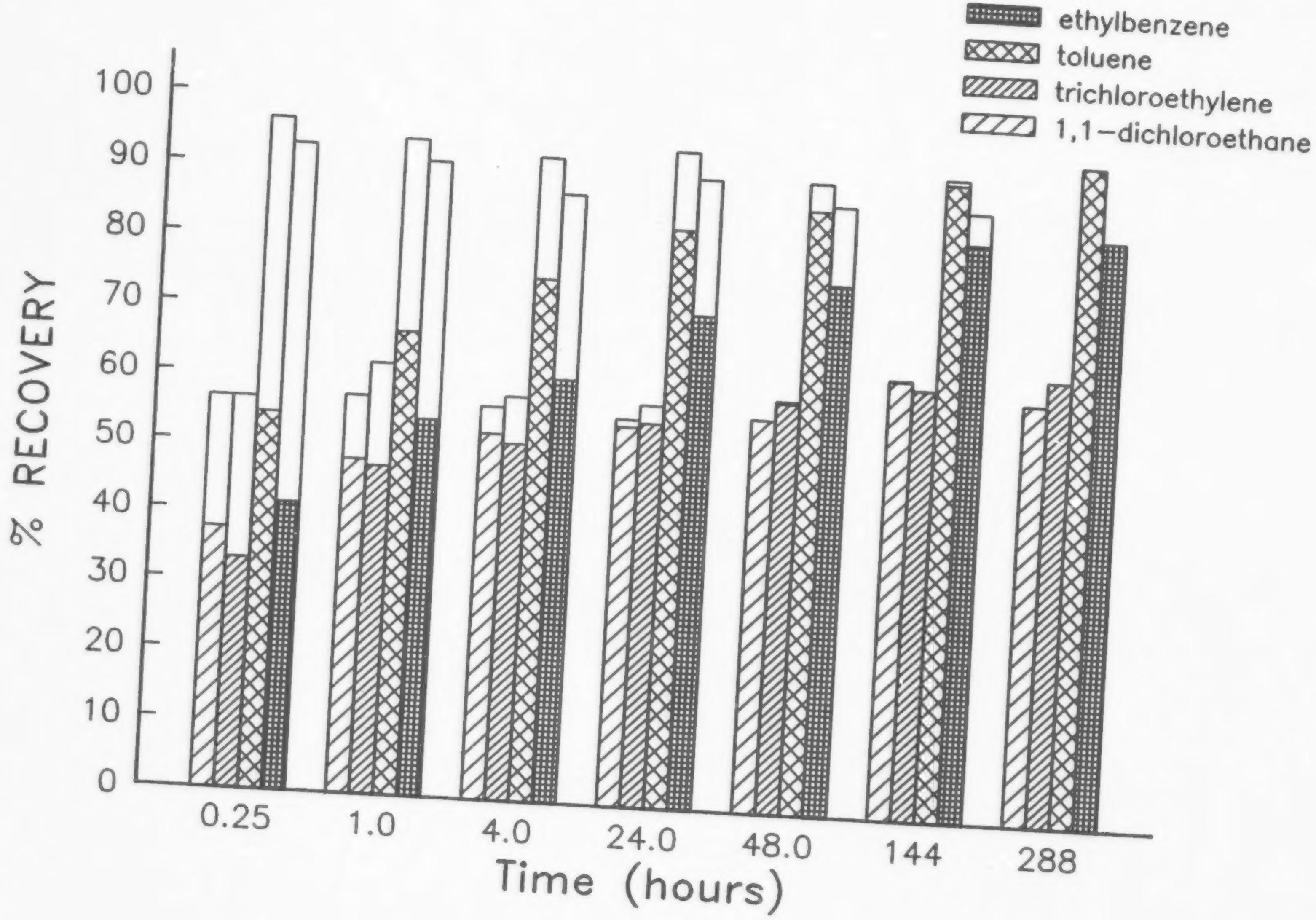


**Figure 1.** **Total and 22C (hatch marked) recoveries of four volatile organic contaminants from a sludge treated loamy sand soil.**

## Plant Uptake of Organic Contaminants

Preliminary greenhouse studies have been conducted to investigate plant uptake of organic contaminants. Ryegrass was grown in microcosms in sludge treated soil contaminated with 14C-labelled compounds (one compound per microcosm). The microcosms are closed, 10 cm diameter stainless steel tubes designed so that the headspace (approximately 4 cm) above the soil column can be evacuated continuously during experiments. Organic compounds and carbon dioxide in the headspace air were collected and analyzed. Ryegrass plants germinated in a potting soil in glass tubes (1 cm i.d.) were inserted through holes (three) in the top of each microcosm and implanted 2 cm into the contaminated soil. Silicone caulking sealed the glass tubes into the microcosm to prevent 14C loss and possible sorption by the growing plant material. Water and nutrients were added as required and the ryegrass grew well and developed a large root mass which explored the complete volume of contaminated soil. At intervals, the grass was harvested and analyzed for 14C. Results to date are variable, as evidenced by 90 and 147% recoveries of 14C from 1,2,4-trichlorobenzene (Table 3). However, they indicate no significant uptake into ryegrass of 14C derived from any of the compounds

TABLE 3. RECOVERIES OF 14C FROM LABELLED COMPOUNDS ADDED TO SLUDGE TREATED SOIL

| | | % Recoveries of 14C | | | |
|---|---|---|---|---|---|
| Compound[a] | Addition (mg) | $CO_2$ | Volatile Organic | Grass | Total |
| 1,24-Trichlorobenzene | 0.44 | 5.8 | 84 | 0.07 | 90 |
| | 1.51 | 3.7 | 144 | 0.13 | 147 |
| Anthracene | 0.68 | 4.9 | 0.00 | 0.00 | 4.9 |
| | 6.68 | 8.2 | 0.01 | 0.05 | 8.3 |
| Benzo(a)pyrene | 2.15 | 0.99 | 0.02 | 0.08 | 1.4 |
| 2,2',5,5'-Tetrachlorobiphenyl | 4.01 | 1.24 | 0.02 | 0.14 | 1.4 |
| Pentachlorophenol | 5.38 | 67 | 0.08 | 0.14 | 67 |

[a] The duration of the experiment with 1,2,4-trichlorobenzene was 50 days and with the other compounds was 126 days.

studied. The results for $14CO_2$ recovery indicated considerable biodegradation of pentachlorophenol, some biodegradation of anthracene and very little biodegradation of benzo(a)pyrene and 2,2',5,5'-tetrachlorobiphenyl, within 126 days. There was no significant volatilization of these compounds or of their degradation products. By contrast, there was considerable volatilization of 1,2,4-trichlorobenzene, or of its organic degradation products. Within 50 days, most of the 14C associated with 1,2,4-trichlorobenzene was recovered on Tenax and a small amount was recovered as $CO_2$.

### Future Research

Information about the persistence of organic contaminants in sludge treated soil and their uptake by plants is required for guideline development to minimize health and environmental hazards resulting from municipal sludge use in agriculture. Experimental techniques to provide such information were developed during the studies described above and the WTC intends to continue these laboratory and greenhouse studies with an expanded range of organic contaminants, soils and plants. The WTC also plans to study the persistence of selected organic contaminants in sludge treated soils under field conditions.

## ORGANIC CONTAMINANT IMPLICATIONS FOR MUNICIPAL SLUDGE UTILIZATION IN AGRICULTURE

Organic contaminants in municipal sludge utilized on agricultural land are subject to a wide variety of physical, chemical and biological processes. They may be volatilized, immobilized by adsorption or transported through the soil column possibly into the groundwater. Assuming normal agricultural management techniques and sludge application rates, transport by leaching or soil migration is probably insignificant (Overcash 1983). Adsorbed organics may be chemically or photochemically degraded, microbially decomposed or desorbed. Research into the behaviour of pesticides indicates that these compounds are sorbed onto organic matter, clay minerals and sesquioxides in soil and that most remain in the plough layer following application (Chang and Page 1978). Information reported for PAH's (McIntyre et al. 1981) and PCB's (Griffin and Chian 1980) in soil indicate that they behave similarly to pesticides.

There is concern that organic contaminants in municipal sludge applied to agricultural land may gain entry to the food chain and affect human and animal health. Current experimental information is inadequate to define what concentrations in sludge represent a significant health hazard. However, sludge is applied to land and there is a need for organic contaminant guidance on its use.

Most pesticides in current use are organic chemicals with toxicities of the same orders of magnitude as the organic contaminants in sludge (Naylor and Loehr 1982). Consequently, it has been suggested (Jacobs and Zabik 1984) that organic contaminant applications in sludge at pesticide application rates would probably be acceptable. Normal pesticide application rates range from 0.3 up to 3-4 kg $ha^{-1}$. Assuming an agronomic application rate of 5-10 tonnes $ha^{-1}$ dw, sludge containing 100 mg $kg^{-1}$ dw of an organic contaminant would apply 0.5-1 kg of contaminant $ha^{-1}$. Jacobs and Zabik (1984) concluded that "concentrations of an organic approaching 100 mg $kg^{-1}$ dw must be viewed as potentially having an impact on the soil-plant system, depending on the nature of that organic chemical". Assuming this criterion, and that the data presented in Table 2 are representative, it appears that Canadian (including Ontario) sludges represent little risk to the soil-plant system. Phthalate esters were the main organic contaminants which exceeded 100 mg $kg^{-1}$ dw in sludges and they are readily degradable in soil (Huddleston et al. 1986 and Ryan 1986).

Naylor and Loehr (1982) pursued a different approach than Jacobs and Zabik (1984) but drew similar conclusions. Evidence was presented that (a) organic contaminants in sludge have acute toxicities similar to pesticides and household chemicals and (b) assuming agronomic sludge application rates, the amounts of organic contaminants applied to land are usually substantially less than typical application rates for pesticides. Scenarios developed to compare acute oral doses and maximum acceptable daily doses with amounts of organic contaminants that might be ingested as a consequence of land application of sludge indicated the following. "Except possibly where sludge is consumed in very large amounts, consumption of contaminated soils or crops is not likely to result in ingestion of amounts of organic pollutants exceeding the acceptable daily dose".

Several recent reviews (Kowal 1985; Dean and Seuss 1985; Davis et al. 1984 and Lindsay 1983) have concluded that the most important pathway for transfer of organic contaminants into the foodchain is through contamination of milk following direct ingestion of sludge treated soil by grazing cattle. Fries (1982) calculated that soil ingestion by grazing animals could produce milk-fat residues of 0.7 mg $kg^{-1}$ of PCB's for each mg $kg^{-1}$ dw of PCB's in surface soil. Similarly, Lindsay (1983) presented evidence that, on a worst-case basis, the concentration of residue in milk derived from sludge ingestion would be 0.5 mg $kg^{-1}$ for every 1 mg $kg^{-1}$ dw of residue present in sludge. A no grazing interval of 30 days following sludge spreading was assumed.

Lindsay (1979) reported 37 μg kg$^{-1}$ of dieldrin (normal level ≤1 μg kg$^{-1}$) in the whole milk of cattle grazing land in the UK which had received sludge containing 17 mg kg$^{-1}$ dw of dieldrin. The dieldrin was employed as a fungicide in carpet manufacture and occurred in the factory effluent. Similarly, Scheltinga (1984) reported contamination of milk with dieldrin as a result of grazing land in the Netherlands which had received sludge containing as much as 20 mg kg$^{-1}$ dw of dieldrin. Rundle et al. (1982) reported dieldrin levels from 1-1.5 μg kg$^{-1}$ in milk from cattle kept on a sludge disposal farm in the UK. Majeti and Clark (1981) reported 5 mg kg$^{-1}$ of PCB's in milk fat (acceptable limit 1.5 mg kg$^{-1}$ and PCB contamination in ground beef from cattle grazing land near Bloomington, Indiana which had received sludge containing as much as 300 mg kg$^{-1}$ dw of PCB's.

Although few in number, the incidents cited above indicate that contamination of the food chain may result from land application of municipal sludge. The likelihood of such incidents occurring in Canada is thought to be small since sludge application rates are controlled and measurements indicate that Canadian sludges have low concentrations of organic contaminants. In each of the cases cited above, the contamination resulted from direct ingestion of sludge by cattle following surface application on pasture land. The author is not aware of food chain contamination following sludge incorporation into soil.

## Summary and Recommendations

Based on the limited organic contaminant data available it is suggested that land application of Canadian municipal sludges probably does not represent a significant hazard to the food chain. The concentrations in sludge generally were <10 mg kg$^{-1}$ dw and organic contaminant application rates to land would be less than current pesticide application rates. Phthalate esters in several sludges exceeded 10 mg kg$^{-1}$ dw but they are readily degradable in soil. However, additional information will be required to satisfy public concerns about organic contaminants in sludge applied to agricultural land. Research must be continued to: (1) develop reliable analytical techniques for sludge, (2) increase the organic contaminant data base for sludges and (3) obtain more information about the fates of organic contaminants in sludge applied to agricultural land.

Until additional information is obtained, it is suggested that the following preliminary organic contaminant guidelines be observed for sludge utilization in Canada. (a) Periodic analysis for organic contaminants should be conducted on Canadian sludges for utilization on agricultural land. (b) Sludges containing ≤100 mg kg$^{-1}$ dw of individual phthalate esters or ≤10 mg kg$^{-1}$ dw of any other base-neutral or acid organic contaminant may be applied to pasture and arable land according to existing Canadian sludge use guidelines. (c) Application on pasture land of sludges containing >100mg $kg^{-1}$ dw of individual phthalates esters or >10 mg $kg^{-1}$ dw of any other base-neutral or acid organic contaminant and on arable land of sludges containing >1000 mg $kg^{-1}$ dw of individual phthalate esters or >100 mg $kg^{-1}$ of any other base-neutral or acid organic contaminant, should be subject to approval based on a consideration of the degree of toxicity and persistence of the contaminant.

## REFERENCES

**Chang, A.C. and Page, A.L. 1978.** Toxic Chemicals Associated with Land Treatment of Wastewater. Pages 47-57 in H.L. McKim ed. State of Knowledge in Land Treatment of Wastewater, Vol. I, U.S. Army Corps of Engineers, CRREL, Hanover, New Hampshire.

**Davis, R.D., Howell, K., Oake, R.J., and Wilcox, P., 1984.** Significance of organic contaminants in sewage sludges used on agricultural Land. Pages 73-79 in Proceedings of International Conference on Environmental Contamination. Imperial College, London, July 1984. CEP Consultants, Edinburgh, UK.

**Dean, R.B., and Seuss, M.J., 1985.** The risk to health of chemicals in sewage sludge applied to land. Waste Management and Res. 3: 251-278.

**EPA/FDA/USDA, 1981.** Land Application of Municipal Sludge for the Production of Fruits and Vegetables - A Statement of Federal Policy and Guidance. US Environmental Protection Agency Joint Policy Statement SW-905.

**Federal Register, 1979.** Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations. Part III 40 Code of Federal Regulations 136, Vol. 44(322): 69464 (Dec. 3, 1979).

**Fries, G.F. 1982.** Potential polychlorinated biphenyl residues in animal products from application of contaminated sewage sludge to land. J. Environ. Qual. 11: 14-20.

**Griffin, R.A. and Chian, E.S.K. 1980.** Attenuation of Water-Soluble Polychlorinated Biphenyls by Earth Materials. EPA 600/2-80/027. US Environmental Protection Agency, Cincinnati, Ohio.

**Haile, C. and Lopez-Avila, V. 1984.** Development of Analytical List Procedures for the Measurement of Organic Priority Pollutants in Sludge. EPA Report 600/4-84/001. Prepared by Midwest Research Institute, Kansas City, Mo.

**Huddleston, R.L., Bleckmann, C.A., and Wolfe, J.R. 1986.** Land treatment biological degradation processes. Pages 41-61 in R.C. Loehr and J.F. Malina, Jr. eds. Land Treatment - A Hazardous Waste Management Alternative. Water Resources Symposium Number Thirteen, The Univ. of Texas at Austin.

**Jacobs, L.W. and Zabik, M.J. 1984.** Types and concentration of organics in municipal sludge. Pages 3-12 to 3-21 in Proceedings of Municipal Wastewater Sludge Health Effects

Research Planning Workshop, Jan. 10-12, 1984. US Environmental Protection Agency, Cincinnati, Ohio.

**Kowal, N.E. 1985.** Health Effects of Land Application of Municipal Sludge. EPA 600/1-85/015. US Environmental Protection Agency,Cincinnati, Ohio.

**Lindsay, D.G. 1979.** Possible health hazards from the presence of persistent chemical residues in sewage sludge. Pages 238-255 in A.M. Bruce ed. Utilization of Sewage sludge on Land. Proceedings of a Water Research Centre, Conference held at Oxford. Water Research Centre, Medmenham, UK.

**Lindsay, D.G. 1983.** Effects arising from the presence of persistent organic compounds in sludge. Pages 19-25 in R.D. Davis et al. eds. Environmental Effects of Organic and Inorganic Contaminants in Sewage Sludge. EUR 8022, D. Reidel Publ. Co.

**Majeti, V.A. and Clark, C.S. 1981.** Health risks of organics in land application. Journ. Amer. Soc. Civil Eng. 107(EE2): 339-357.

**McIntyre, A.E., Perry, R. and Lester, J.N. 1981.** Analysis of polynuclear aromatic hydrocarbons in sewage sludges. Anal. Letters 14: 291-309.

**MISA, 1986.** Municipal - Industrial Strategy for Abatement (MISA). MISA White Paper. June 1986. Ontario Ministry of the Environment, Toronto.

**MISA, 1988.** Thirty Seven Municipal Water Pollution Control Plants: Pilot Monitoring Study. Volume I, interim report. December 1988. Ontario Ministry of the Environment, Toronto.

**Naylor, L.M. and Loehr, R.C. 1982.** Priority pollutants in municipal sewage sludge. Biocycle 23(4): 18-22 and 23(6): 37-42.

**Overcash, M.R. 1983.** Land treatment of municipal effluent and sludge: specific organic compounds. Pages 199-231 in A.L. Page et al., eds. Proceedings of the 1983 Workshop on Utilization of Municipal Wastewater and Sludge on Land. Univ. of Calif., Riverside.

**Rundle, H., Calcroft, M. and Holt, C. 1982.** Agricultural disposal of sludges on a historic sludge disposal site. Water Pollut. Control 81: 619-632.

**Ryan, J.R. 1986.** The land treatability of appendix VIII organics presented in petroleum industry wastes. Pages 347-367 in R.C. Loehr and J.F. Malina Jr. eds. Land Treatment - A Hazardous Waste Management Alternative. Water Resources Symposium Number Thirteen, The Univ. of Texas at Austin.

**Scheltinga, H.M.J. 1984.** Agricultural use of sewage sludge in the Netherlands. In D. Calamari, ed. Prevention of Pollution by Substances Derived from Wastes. Proceedings of a Commission of the European Communities Conference, Rome.

**Taylor, D. 1984.** Managing organics in sludge reuse programs. BioCycle, 25(6): 20-22.

**Warner , J.S., G.A. Jungclaus, T.M. Engel, R.M. Riggin, and C.C. Chuang, 1980.** Analytical Procedures for Determining Organic Priority Pollutants in Municipal Sludges. EPA 600/2-80/030. US Environmental Protection Agency, Cincinnati, Ohio.

**Webber M.D. and S. Lesage, 1989.** Organic contaminants in Canadian Municipal Sludges. Waste Management & Research 7: 63-82.

# MODELS FOR PREDICTING THE FATE OF HAZARDOUS CONTAMINANTS IN WASTEWATER TREATMENT PLANTS

John Bell, Doug Thompson, Jeff Kemp
Enviromega Ltd.

Henryk Melcer
Environment Canada

Hugh Monteith
Ontario Ministry of the Environment

## ABSTRACT

Computer based steady state and dynamic models were developed for predicting the fate of hazardous compounds in wastewater treatment plants. The models were calibrated by fitting the treatability parameters for selected compounds using data from an activated sludge pilot plant and a bench scale activated sludge system. The pilot plant was fed with wastewater from two different municipal sources. The pilot plant was operated in parallel with a municipal treatment plant and was found to adequately simulate the performance of the full scale plant. Steady state model predictions were compared with data from two pilot plants, a full scale municipal plant, and three petroleum refinery wastewater treatment plants. The model produced reasonably accurate predictions of the fate of nonchlorinated aromatic hydrocarbons and somewhat less accurate predictions for chlorinated hydrocarbons. The dynamic model appeared to predict the trend of the observed effluent concentrations for three chlorinated hydrocarbons but tended to underestimate the concentrations. The results suggest that the current models, calibrated with pilot plant data, may produce useful predictions of the fate of hazardous compounds in full scale plants.

## 1. INTRODUCTION

Computer based steady state and dynamic models for predicting the fate of hazardous contaminants in wastewater treatment plants were developed. The objective of the present work was to test the models against existing full scale and pilot plant data. The treatability data base used by the models to calculate the required kinetic parameters was modified to incorporate Henry's law coefficients and biodegradation rate constants obtained by fitting the models to data from pilot plant tests carried out at Environment Canada's Wastewater Technology Centre (WTC). Testing of the models was carried out on selected volatile organic compounds (VOCs) using the modified data base.

The steady state model was tested against data from the following sources:

WTC Pilot Plant (Thompson et al., 1989),
U.S. EPA Pilot PLant (Govind et al., 1989)
Highland Creek WPCP (Thompson et al., 1989)
Petro-CanadaRefinery(CanviroConsultants,1987)
Petro-Canada Refinery (Environment Canada, 1988)
Esso Refinery (Canviro Consultants, 1987)
Montreal East Refinery (IEC Beak Consultants Ltd., 1985)

The dynamic model was tested against data from the Galt WPCP (Canviro Consultants, 1988).

## 2. DESCRIPTION OF MODELS

### 2.1 Introduction

It is possible for hazardous contaminants to be removed from the wastewater in a biological treatment plant by several different mechanisms. The removal mechanisms generally considered to be most significant are biodegradation, volatilization, and sorption. Other mechanisms are possible, such as photolysis, hydrolysis, or other chemical reactions. These chemical reaction mechanisms may be important removal pathways for specific compounds but in practice are difficult to separate from biodegradation. In the present models individual degradation reactions are not considered, and the degradation mechanism is assumed to be biodegradation.

In the models, removal of hazardous contaminants is considered to take place by a combination of biodegradation, volatilization, and sorption onto suspended solids. Not all of these mechanisms are important for all compounds. For example, heavy metals would be removed only by sorption (or precipitation which might be indistinguishable from sorption). Volatile organic compounds may be removed mainly by biodegradation and volatilization, with sorption being a less important removal mechanism. Some hydrophobic organic compounds may be removed to a significant extent by all three mechanisms.

## 2.2 Biodegradation

To develop a mechanistic model of the contaminant removal process, suitable mathematical expressions for the rates of removal by the different mechanisms are required. A number of mathematical expressions have been used to describe the rate of biodegradation of organic compounds (e.g., the Monod equation). Hazardous contaminants are generally present at low concentrations in municipal wastewater treatment plants. At low substrate concentrations, it has been demonstrated that the biodegradation rate can be expressed as a pseudo first order reaction. In fact, the Monod equation and other rate expressions can be approximated by a pseudo first order rate expression at low substrate concentration. The form of the rate expression for low substrate concentration is,

$$r_b = k'_b XC \tag{1}$$

where

$r_b$ = biodegradation rate, ug/L/h,
$k'_b$ = biodegradation rate constant, L/mg/h,
$X$ = biomass concentration, mg/L,
$C$ = contaminant concentration, ug/L.

In most activated sludge systems the biomass concentration, X, is maintained at a relatively constant concentration. With X constant, Equation 1 becomes a first order rate equation,

$$r_b = k_b C \tag{2}$$

where

$k_b = k'_b X$ = pseudo first order rate constant, $h^{-1}$.

## 2.3 Volatilization

Volatile contaminants may be removed from wastewater by volatilization into the atmosphere. Even contaminants not normally considered to be volatile can be substantially removed by volatilization if they are highly hydrophobic. Volatilization of contaminants to the atmosphere may occur from the surface of open tanks such as clarifiers. The majority of volatilization, however, occurs through air stripping in aerated process vessels. Both volatilization from the surface of the process vessels and stripping in aerated tanks are included in the models.

### 2.3.1 Surface Volatilization

The rate of volatilization from the surface of a basin is given by,

$$r_v = K_L a(C - C^*) \tag{3}$$

where

$r_v$ = rate of volatilization, ug/L h,
$K_L$ = overall mass transfer coefficient, m/h,
a = specific interfacial surface area, $m^2/m^3$,
C = concentration of volatile compound in the water, ug/L,
$C^*$ = equilibrium concentration of compound in water, ug/L.

For a basin of uniform water depth, the specific interfacial area is equal to the reciprocal of the basin depth. We may assume that the air movement above the basin is sufficient to carry the volatilized compounds away so that their bulk concentration in the air phase is negligible. In that case the equilibrium water phase concentration will also be negligible. Therefore equation 3 becomes,

$$r_v = K_L C/h \tag{4}$$

or

$$r_v = k_v C \tag{5}$$

where

h = basin depth, m,
$k_v = K_L/h$ = volatilization rate constant , $h^{-1}$.

The mass transfer coefficients for surface volatilization can be estimated using correlations such as those developed by Mackay and Yeun (1983):

### 2.3.2 Air Stripping

Surface Aeration

Process vessels may be aerated by either submerged diffusers or mechanical surface aerators. For surface aeration the contaminant removal rate by stripping is given by,

$$r_s = K_L a(C - C^*) \tag{6}$$

where

$r_s$ = stripping rate, ug/L h,
$K_L$ = overall mass transfer coefficient, m/h,

$a$ = specific interfacial area for mass transfer, $m^2/m^3$,
$C^*$ =equilibrium concentration of contaminant in water, ug/L.

For surface aeration systems the equilibrium concentration, $C^*$, can be assumed to be zero since the atmosphere around the aerator is considered to be free of the volatilizing compound. Equation 6 can then be rewritten as,

$$r_s = k_s C \tag{7}$$

where

$k_s = K_L a$ = stripping rate constant, $h^{-1}$.

The overall mass transfer coefficient can be obtained from the liquid phase and gas phase mass transfer coefficients,

$$K_L = (1/k_L + 1/(k_G H))^{-1} \tag{8}$$

where

$k_L$ = liquid phase mass transfer coefficient, m/h,
$k_G$ = gas phase mass transfer coefficient, m/h,
$H$ = Henry's law coefficient, dimensionless.

The liquid phase mass transfer coefficient for surface aeration can be related to the oxygen transfer coefficient,

$$k_L = K_L^{oxy}(D_c/D_{oxy})^n \tag{9}$$

where

$k_L^{oxy}$ = oxygen transfer coefficient, $h^{-1}$,
$D_c$ = diffusion coefficient of compound in water, $cm^2/s$,
$D_{oxy}$ = diffusion coefficient of oxygen in water, $cm^2/s$.
$n$ = proportionality parameter between 0.5 and 1.0.

Combining equation 9 with a correlation for the oxygen transfer rate constant, the following equation, proposed by Thibodeaux (1979), was used to estimate the liquid phase mass transfer coefficient for mechanical surface aeration:

$$k_L a = 109.39 N_{oxy} E P f (1.024)^{(T-20)} (D_c/D_{oxy})^{0.5}/V \tag{10}$$

where

$N_{oxy}$ = standard oxygen transfer rate for aerator, kg/kW h,
$E$ = power delivery efficiency for aerator, dimensionless,
$P$ = aerator power, kW,
$f$ = dirty water/clean water conversion factor, dimensionless,
$T$ = temperature, °C,

$V$ = volume of aeration basin, $m^3$.

To determine the overall mass transfer coefficient, the gas phase mass transfer coefficient must be estimated. Munz and Roberts (1984) suggest a value of 20 for the ratio of the gas and liquid phase mass transfer coeffients, i.e.,

$$k_G/k_L = 20 \tag{11}$$

Combining Equations 8 and 11 yields,

$$K_La = 20Hk_La/(20H + 1) \tag{12}$$

Subsurface Aeration

For subsurface aeration, the rate of stripping is estimated by the following equation proposed by (Matter-Muller et al. (1981):

$$r_s = Q_GH[1 - \exp(-K_La/HQ_G)]C \tag{13}$$

where

$Q_G$ = air flow rate per unit wastewater volume, $m^3/m^3/h$,

For a given system, with a constant aeration rate, all of the terms on the right hand side of Equation 13 except C are reasonably constant. Therefore, Equation 13 can be rewritten as,

$$r_s = k_sC \tag{14}$$

where

$k_s = Q_GH[1 - \exp(-K_La/HQ_G)]$, $h^{-1}$.

For subsurface aeration, the value of $k_La$ for the volatile compound can be estimated from Equation 9 using the $K_La$ for oxygen under the same conditions. For subsurface aeration, a value of $n = 1.0$ was used in Equation 9. The overall mass transfer coefficient for the compound is then calculated from Equation 12. The $K_La$ for oxygen for a diffused air system can be measured or calculated from the oxygen transfer efficiency.

## 2.4 Sorption

Removal of a contaminant by sorption can be expressed in terms of the concentration of the contaminant on the suspended solids and the solids wasting rate. In a liquid/solid system, at equilibrium, the concentration of a contaminant on a solid sorbent can be expressed by,

$$q = K_pC \tag{15}$$

where

$q$ = concentration of contaminant in solid phase, ug/g,
$K_p$ = sorption partition coefficient, L/g,
$C$ = concentration of contaminant in liquid phase, ug/L.

Equation 15 is generally valid at low contaminant concentrations such as encountered in municipal treatment plants.

The sorption partition coefficient for a given compound can be related to the octanol/water partition coefficient of that compound. The following correlation, reported by Dobbs _et al._ (1986), was used to estimate the sorption partition coefficients:

$$\log K_p = 0.6 \log K_{ow} + 1.06 \qquad (16)$$

where

$K_{ow}$ = octanol/water partition coefficient, dimensionless.

The partition coefficient obtained from Equation 16 provides the solid phase contaminant concentration on a volatile solids basis and was used for both primary and secondary solids.

Sorption of contaminants by sewage treatment plant solids has been observed to be a relatively rapid process. It was therefore assumed that sorption equilibrium is attained instantaneously.

In the activated sludge system, contaminants can be removed from the wastewater by sorption onto primary and secondary solids. The current model assumes that primary and secondary solids are discharged separately. For the secondary solids, removal of contaminants by sludge wasting and carryover of solids in the plant effluent are both accounted for.

The removal rate of a contaminant by sorption in the primary clarifier can be expressed as,

$$r_a^{PC} = QX_{in}mK_pC/V_{PC} = k_a^{PC}C \qquad (17)$$

where

$r_a^{PC}$ = rate of contaminant removal by sorption, ug/L h,
$Q$ = wastewater flow rate, $m^3/h$,
$X_{in}$ = influent volatile suspended solids concentration, mg/L,
$m$ = fraction of suspended solids removed in primary clarifier,
$V_{PC}$ = volume of primary clarifier, $m^3$,
$k_a^{PC}$ = $QX_{in}mK_p/V_{PC}$ = sorption rate constant in primary clarifier, $h^{-1}$.

The removal rate of a contaminant by sorption on suspended solids carried over in the secondary clarifier effluent can be expressed as,

$$r_a^{sc} = QX_{eff}K_p/V_{sc} = k_a^{sc}C \qquad (18)$$

where

$r_a^{sc}$ = rate of contaminant removal by sorption, ug/L h,
$X_{eff}$ = effluent volatile suspended solids concentration, mg/L,
$V_{sc}$ = volume of secondary clarifier, $m^3$,
$k_a^{sc}$ = $QX_{eff}K_p/V_{sc}$ = sorption rate constant in secondary clarifier, $h^{-1}$.

## 2.5 Steady State Model

The fractional removal of each compound in each unit operation, under steady state conditions, was calculated from the appropriate mass balance equation. In the current model, the grit chamber, primary clarifier, and secondary clarifier are treated as completely mixed, continuous stirred tank reactors (CSTRs).

The aeration basin is treated as one to ten CSTRs of equal volume in series with sludge recycle to the first reactor. The biomass concentration was assumed to be equal in all reactors and all biomass growth was assumed to take place in the first reactor. The biomass growth rate was set equal to the activated sludge wasting rate. It was further assumed that sorption and desorption take place instantaneously and therefore that equilibrium with respect to sorption and desorption exists at all times, at every point in the system.

## 2.6 Dynamic Model

For the dynamic modelling, unsteady state mass balance equations were written for each unit operation. The set of differential equations were solved for the final plant effluent concentration as a function of time, given a set of plant influent concentrations and flow rates as a function of time. The differential equations were solved numerically using a fifth order Runge-Kutta technique. Initial concentrations for the solution were estimated using the starting influent concentration and a steady state mass balance.

# 3. DATA BASE DEVELOPMENT

## 3.1 Introduction

Data from pilot plant tests carried out at Environment Canada's Wastewater Technology Centre (Thompson et al., 1989) were used to develop treatability parameters for the predictive models.

The pilot plant data was used to determine Henry's law coefficients and biodegradation rate constants for seven VOCs. These parameters were incorporated into the existing treatability data base developed for use with the computer based models.

## 3.2 Henry's Law Coefficients

Henry's law coefficients were fitted to the pilot plant data using linear regression of the following equation:

$$C_g = HC_e \tag{19}$$

where

$C_g$ = aeration tank off-gas VOC concentration, ug/L,
$C_e$ = aeration tank effluent VOC concentration, ug/L,
$H$ = Henry's law coefficient, dimensionless.

Henry's law coefficients for seven VOCs were determined. Table 3.1 gives the fitted Henry's law coefficients compared with values obtained from the literature.

Table 3.1 Henry's Law Coefficients

| Compound | Fitted Henry's Law Coefficient (Dimensionless) | Literature Henry's Law Coefficient (Dimensionless) |
|---|---|---|
| Chloroform | 0.031<br>(0.016 - 0.046) | 0.14 |
| Dichloromethane | 0.052<br>(0.032 - 0.072) | 0.13 |
| 1,4-Dichlorobenzene | 0.089<br>(0.066 - 0.111) | 0.11 |
| Tetrachloroethylene | 0.216<br>(0.146 - 0.286) | 1.19 |
| Trichloroethylene | 0.201<br>(0.146 - 0.257) | 0.38 |
| 1,1,1-Trichloroethane | 0.209<br>(0.159 - 0.259) | 0.20 |
| p-Xylene | 0.372<br>(-0.159 - 0.904) | 0.22 |

Note: 95% confidence limits given in parentheses

Of the seven compounds, one has a fitted Henry's law coefficient greater than the literature value (p-xylene). However, since the confidence limits for the fitted value include the literature value, it cannot be concluded that the fitted value is different from the literature value. The fitted coefficient for 1,1,1-trichloroethane is approximately equal to the literature value. The remaining five compounds have fitted Henry's law coefficients less than the corresponding literature values. The fitted value for 1,4-dichlorobenzene is close to the literature value and the confidence limits include the literature value.

### 3.3 Biodegradation Rate Constants

Biodegradation rate constants were fitted to the pilot plant data using linear regression of the following rate equation:

$$r_b = k_b 1.02^{(T-20)} X C_e V \tag{20}$$

where

$r_b$ = rate of biodegradation, ug/h,
$k_b$ = biodegradation rate constant, L mg$^{-1}$h$^{-1}$,
$T$ = wastewater temperature, °C,
$X$ = mixed liquor volatile suspended solids concentration, mg/L,
$C_e$ = effluent contaminant concentration, ug/L,
$V$ = aeration tank volume, L.

The rate of biodegradation was determined by mass balance as follows:

$$r_b = QC_i - Q_g C_g - Q_w C_w - QC_e \tag{21}$$

where

$Q$ = wastewater flow rate, L/h,
$C_i$ = influent contaminant concentration, ug/L,
$Q_g$ = off-gas flow rate, L/h,
$C_g$ = off-gas contaminant concentration, ug/L,
$Q_w$ = waste sludge flow rate, L/h,
$C_w$ = waste sludge contaminant concentration, ug/L,

Since biodegradation was not measured directly but was assumed from a mass balance difference, it cannot be stated conclusively that the disappearance of any compound was the result of biodegradation. However, since no other mechanisms are known to account for the disappearance, the mechanism was assumed to be biodegradation.

Table 3.2 gives the fitted biodegradation rate constants together with rate constants determined by the U.S. Environmental Protection Agency from pilot plant tests (Govind et al., 1989). Govind et al. (1989) reported pseudo first order rate constants and did not report the mixed liquor volatile suspended solids (MLVSS) concentrations. To obtain biodegradation rate constants for comparison, an MLVSS concentration of 2000 mg/L was assumed.

Table 3.2 Biodegradation Rate Constants

| Compound | WTC Biodegradation Rate Constant (L mg$^{-1}$ h$^{-1}$) | EPA Biodegradation Rate Constant (L mg$^{-1}$ h$^{-1}$) |
|---|---|---|
| Chloroform | 1.07E-4<br>(6.62E-5 - 1.48E-4) | 6.97E-5 |
| Dichloromethane | 2.21E-4<br>(1.12E-4 - 3.30E-4) | 1.13E-4 |
| 1,4-Dichlorobenzene | 3.27E-5<br>(-5.00E-5 - 1.15E-4) | 1.19E-3 |
| Tetrachloroethylene | 3.54E-4<br>(1.51E-5 - 6.92E-4) | --- |
| Trichloroethylene | 3.98E-4<br>(-1.12E-4 - 9.07E-4) | 1.46E-4 |
| 1,1,1-Trichloroethane | 6.37E-4<br>(-5.01E-5 - 1.32E-3) | --- |
| p-Xylene | 7.42E-3<br>(-1.80E-2 - 3.29E-2) | 2.60E-3 |

Note: 95% confidence limits given in parentheses

Four of five of the EPA biodegradation rate constants are included within the confidence limits of the WTC rate constants suggesting reasonable agreement between the two sets of data. The rate constant for 1,4-dichloromethane determined by the EPA is almost two orders of magnitude higher than that determined by WTC.

The confidence limits for four compounds include zero, therefore it cannot be concluded with 95% confidence that those compounds were biodegraded. For p-xylene it seems likely that biodegradation did take place, however the scatter in the data resulted in wide confidence limits. Additional testing with single compounds at higher dose levels should be carried out to confirm the biodegradation kinetics.

## 4. RESULTS AND DISCUSSION

### 4.1 Introduction

The steady state model was tested against data from the following sources:

WTC Pilot Plant (Thompson et al., 1989),
U.S. EPA Pilot Plant (Govind et al., 1989)
Highland Creek WPCP (Thompson et al., 1989)
Petro-CanadaRefinery(CanviroConsultants,1987)
Petro-Canada Refinery (Environment Canada, 1988)

Esso Refinery (Canviro Consultants, 1987)
Montreal East Refinery (IEC Beak Consultants Ltd., 1985)

The dynamic model was tested against data from the Galt WPCP (Canviro Consultants, 1988).

Plant operating and design parameters were obtained from the listed sources. In some cases, required parameters were calculated or estimated from reported information where the required parameters were not specifically reported.

## 4.2 Steady State Model

### 4.2.1 WTC Pilot Plant

Data obtained from the WTC pilot plant (Thompson et al., 1989) were compared to the steady state model predictions. Table 4.1 gives the general design and operating parameters of the pilot plant. Table 4.2 gives the specific operating variables for each experiment. Tables 4.3 - 4.9 give the observed and predicted removal by stripping and biodegradation for the seven compounds tested. In some cases, a negative value for percent biodegradation was obtained from the mass balance. In those cases, the percent biodegradation is reported as zero in the tables and on the graphs. The negative values were used in fitting the biodegradation rate constants, however.

Table 4.1 WTC Pilot Plant Design and Operating Parameters

| | |
|---|---|
| Secondary Clarifier Surface Area ($m^3$) | 1.2 |
| Secondary Clarifier Depth (m) | 2.0 |
| Aeration Basin Volume ($m^3$) | 5.0 |
| Aeration Basin Depth (m) | 2.7 |
| Aeration Basin Hydraulics | 1 CSTR |
| Type of Aeration | Subsurface |
| Air Flow Rate ($m^3$/h) | 9.7 - 49.5 |
| Oxygen Transfer Efficiency (%) | 2.0 - 5.2 |
| Dissolved Oxygen Concentration (mg/L) | 0.4 - 6.3 |
| MLVSS Concentration (g/L) | 2.0 - 3.2 |
| Wastewater Temperature (°C) | 17.5 - 25.5 |
| Wastewater Flow Rate ($m^3$/h) | 0.81 |
| Secondary Sludge Wasting Rate ($m^3$/d) | 0.27 |
| Sludge Recycle Ratio (%) | 37 |

Table 4.2 Operating Parameters for WTC Pilot PLant Experiments

| Experiment Number | Diffuser Type | Air Flow ($m^3/h$) | MLVSS (g/L) | Temperature (°C) |
|---|---|---|---|---|
| 1 | Coarse | 19.5 | 2.0 | 19.0 |
| 2 | Coarse | 38.4 | 2.0 | 18.0 |
| 3 | Coarse | 11.7 | 2.0 | 18.0 |
| 4 | Coarse | 38.8 | 2.0 | 18.0 |
| 5 | Fine | 28.9 | 2.0 | 20.0 |
| 6 | Fine | 9.7 | 2.0 | 20.0 |
| 7 | Fine | 28.8 | 2.0 | 25.5 |
| 8 | Coarse | 11.6 | 2.0 | 25.0 |
| 9 | Coarse | 12.1 | 2.0 | 19.0 |
| 10 | Coarse | 38.0 | 2.0 | 20.5 |
| 11 | Coarse | 38.2 | 2.0 | 20.5 |
| 12 | Fine | 12.3 | 3.2 | 19.0 |
| 13 | Coarse | 48.7 | 3.2 | 23.0 |
| 14 | Coarse | 16.1 | 3.2 | 20.5 |
| 15 | Coarse | 49.5 | 3.2 | 19.5 |
| 16 | Fine | 37.4 | 3.2 | 17.5 |
| 17 | Coarse | 16.0 | 3.2 | 18.5 |

Table 4.3 WTC Pilot Plant Modelling - Chloroform

| Experiment Number | Observed % Stripped | Observed % Biodegraded | Predicted % Stripped | Predicted % Biodegraded |
|---|---|---|---|---|
| 1 | 13.9 | 49.0 | 24.1 | 42.7 |
| 2 | 24.2 | 61.4 | 38.5 | 34.6 |
| 3 | 64.7 | 0.0 | 16.0 | 47.3 |
| 4 | 77.2 | 9.5 | 38.7 | 34.5 |
| 5 | 34.9 | 25.6 | 32.0 | 38.3 |
| 6 | 35.0 | 39.0 | 13.7 | 48.6 |
| 7 | 34.3 | 57.0 | 32.0 | 38.3 |
| 8 | 27.7 | 45.1 | 15.9 | 47.4 |
| 9 | 34.5 | 41.2 | 16.4 | 47.1 |
| 10 | 33.5 | 60.4 | 38.2 | 34.8 |
| 11 | 39.9 | 32.4 | 38.4 | 34.7 |
| 12 | 14.9 | 73.4 | 13.0 | 58.4 |
| 13 | 18.3 | 73.3 | 37.1 | 42.2 |
| 14 | 28.6 | 51.3 | 16.4 | 56.1 |
| 15 | 69.0 | 18.5 | 37.5 | 42.0 |
| 16 | 48.9 | 36.0 | 31.2 | 46.2 |
| 17 | 65.2 | 1.4 | 16.3 | 56.2 |

Table 4.4 WTC Pilot Plant Modelling - Dichloromethane

| Experiment Number | Observed | | Predicted | |
|---|---|---|---|---|
| | % Stripped | % Biodegraded | % Stripped | % Biodegraded |
| 1 | 19.5 | 55.6 | 25.0 | 54.7 |
| 2 | 52.8 | 19.3 | 39.6 | 44.0 |
| 3 | 37.2 | 22.6 | 16.7 | 60.7 |
| 4 | 91.6 | 0.0 | 39.9 | 43.8 |
| 5 | 9.9 | 74.9 | 33.1 | 48.8 |
| 6 | 20.7 | 46.7 | 14.3 | 62.5 |
| 7 | 32.8 | 57.7 | 33.1 | 48.8 |
| 8 | 221.4 | 0.0 | 16.5 | 60.8 |
| 9 | 14.5 | 79.4 | 17.1 | 60.4 |
| 10 | 29.7 | 67.8 | 39.4 | 44.2 |
| 11 | 103.0 | 0.0 | 39.5 | 44.1 |
| 12 | 7.5 | 87.6 | 12.8 | 70.7 |
| 13 | 85.1 | 1.8 | 36.7 | 51.3 |
| 14 | 25.1 | 64.6 | 16.1 | 68.0 |
| 15 | 31.1 | 65.8 | 37.0 | 51.1 |
| 16 | 28.1 | 67.0 | 30.8 | 56.1 |
| 17 | 23.4 | 69.7 | 16.0 | 68.1 |

Table 4.5 WTC Pilot Plant Modelling - 1,4-Dichlorobenzene

| Experiment Number | Observed | | Predicted | |
|---|---|---|---|---|
| | % Stripped | % Biodegraded | % Stripped | % Biodegraded |
| 1 | 97.7 | 0.0 | 57.6 | 11.2 |
| 2 | 40.1 | 47.0 | 72.3 | 7.3 |
| 3 | 57.4 | 0.0 | 44.7 | 14.6 |
| 4 | 242.7 | 0.0 | 72.5 | 7.2 |
| 5 | 55.2 | 25.3 | 66.7 | 8.8 |
| 6 | 45.0 | 24.1 | 41.0 | 15.6 |
| 7 | 73.9 | 13.8 | 67.1 | 8.7 |
| 8 | 71.5 | 0.0 | 45.0 | 14.5 |
| 9 | 49.3 | 24.6 | 45.6 | 14.4 |
| 10 | 80.1 | 8.0 | 72.6 | 7.2 |
| 11 | 61.0 | 35.6 | 72.7 | 7.2 |
| 12 | 45.6 | 39.3 | 42.1 | 20.3 |
| 13 | 77.9 | 10.8 | 73.8 | 9.1 |
| 14 | 34.8 | 46.0 | 48.3 | 18.1 |
| 15 | 114.6 | 0.0 | 73.7 | 9.2 |
| 16 | 81.1 | 8.6 | 68.4 | 11.0 |
| 17 | 80.1 | 0.0 | 48.0 | 18.2 |

Table 4.6 WTC Pilot Plant Modelling - Tetrachloroethylene

| Experiment Number | Observed % Stripped | Observed % Biodegraded | Predicted % Stripped | Predicted % Biodegraded |
|---|---|---|---|---|
| 1 | 25.7 | 70.0 | 44.6 | 44.5 |
| 2 | 61.4 | 27.9 | 59.8 | 32.3 |
| 3 | 82.3 | 0.0 | 32.0 | 54.7 |
| 4 | 196.3 | 0.0 | 59.9 | 32.2 |
| 5 | 111.9 | 0.0 | 54.0 | 37.0 |
| 6 | 135.5 | 0.0 | 31.1 | 55.4 |
| 7 | 72.1 | 26.0 | 56.2 | 35.2 |
| 8 | 34.4 | 54.9 | 33.7 | 53.3 |
| 9 | 72.3 | 18.8 | 32.9 | 53.9 |
| 10 | 101.0 | 0.0 | 61.2 | 31.2 |
| 11 | 22.9 | 73.8 | 61.3 | 31.1 |
| 12 | 63.3 | 27.5 | 27.3 | 62.8 |
| 13 | 39.8 | 56.0 | 57.8 | 36.4 |
| 14 | 97.3 | 0.0 | 31.2 | 59.4 |
| 15 | 104.8 | 0.0 | 56.4 | 37.6 |
| 16 | 105.1 | 0.0 | 51.2 | 42.2 |
| 17 | 118.8 | 0.0 | 30.5 | 60.0 |

Table 4.7 WTC Pilot Plant Modelling - 1,1,1-Trichloroethane

| Experiment Number | Observed % Stripped | Observed % Biodegraded | Predicted % Stripped | Predicted % Biodegraded |
|---|---|---|---|---|
| 1 | 2.6 | 97.0 | 32.5 | 59.9 |
| 2 | 15.7 | 62.5 | 47.1 | 46.7 |
| 3 | 19.0 | 74.6 | 22.0 | 68.9 |
| 4 | 37.0 | 55.2 | 47.3 | 46.5 |
| 5 | 50.7 | 21.5 | 41.3 | 51.9 |
| 6 | 86.1 | 0.0 | 21.2 | 69.6 |
| 7 | 29.6 | 65.0 | 43.3 | 50.0 |
| 8 | 27.3 | 52.2 | 23.3 | 67.8 |
| 9 | 52.8 | 33.5 | 22.7 | 68.2 |
| 10 | 77.3 | 17.0 | 48.5 | 45.4 |
| 11 | 25.3 | 70.4 | 48.7 | 45.3 |
| 12 | 18.1 | 76.8 | 17.8 | 75.8 |
| 13 | 41.1 | 56.6 | 44.4 | 51.3 |
| 14 | 31.4 | 61.8 | 20.9 | 73.0 |
| 15 | 62.8 | 34.1 | 43.0 | 52.6 |
| 16 | 55.0 | 41.4 | 37.8 | 57.3 |
| 17 | 48.1 | 43.2 | 20.3 | 73.5 |

Table 4.8 WTC Pilot Plant Modelling - Trichloroethylene

| Experiment Number | Observed % Stripped | Observed % Biodegraded | Predicted % Stripped | Predicted % Biodegraded |
|---|---|---|---|---|
| 1 | 12.8 | 85.5 | 41.7 | 48.1 |
| 2 | 29.2 | 68.3 | 57.1 | 35.4 |
| 3 | 29.9 | 57.5 | 29.5 | 58.1 |
| 4 | 132.8 | 0.0 | 57.3 | 35.2 |
| 5 | 80.4 | 0.0 | 51.1 | 40.3 |
| 6 | 73.0 | 9.7 | 28.1 | 59.3 |
| 7 | 50.3 | 44.3 | 52.9 | 38.9 |
| 8 | 31.2 | 54.5 | 30.8 | 57.0 |
| 9 | 40.5 | 50.0 | 30.4 | 57.4 |
| 10 | 79.4 | 13.9 | 58.3 | 34.4 |
| 11 | 17.3 | 82.7 | 58.4 | 34.3 |
| 12 | 19.4 | 80.6 | 24.5 | 66.5 |
| 13 | 0.0 | 100.0 | 54.7 | 39.9 |
| 14 | 11.0 | 89.0 | 28.5 | 62.9 |
| 15 | 8.7 | 91.3 | 53.5 | 40.9 |
| 16 | 26.9 | 73.1 | 48.0 | 45.8 |
| 17 | 21.3 | 78.7 | 27.9 | 63.5 |

Table 4.9 WTC Pilot Plant Modelling - p-Xylene

| Experiment Number | Observed % Stripped | Observed % Biodegraded | Predicted % Stripped | Predicted % Biodegraded |
|---|---|---|---|---|
| 1 | 2.8 | 97.2 | 5.9 | 93.0 |
| 2 | 4.3 | 95.6 | 10.0 | 88.9 |
| 3 | 2.2 | 97.8 | 3.5 | 95.4 |
| 4 | 27.7 | 72.3 | 10.0 | 88.9 |
| 5 | 2.5 | 97.5 | 8.3 | 90.6 |
| 6 | 3.3 | 96.7 | 3.8 | 95.1 |
| 7 | 10.7 | 88.8 | 9.6 | 89.4 |
| 8 | 6.2 | 93.8 | 4.0 | 94.9 |
| 9 | 9.6 | 90.4 | 3.6 | 99.0 |
| 10 | 38.3 | 61.7 | 10.9 | 88.0 |
| 11 | 31.9 | 62.1 | 11.0 | 87.9 |
| 12 | 3.4 | 95.6 | 2.9 | 96.4 |
| 13 | 12.7 | 87.3 | 9.1 | 90.1 |
| 14 | 3.8 | 95.8 | 3.2 | 96.0 |
| 15 | 12.4 | 87.6 | 8.3 | 91.0 |
| 16 | 5.9 | 94.1 | 7.1 | 92.2 |
| 17 | 3.9 | 96.1 | 3.1 | 96.2 |

From the tables it can be seen that the best agreement between observed and predicted values was obtained for p-xylene. For all compounds, good agreement between observed and predicted values was obtained for some experiments. For a given experiment, in general, where good agreement was obtained for stripping, good agreement was also obtained for biodegradation. Overall, the predictions appear to be randomly scattered between over and under predictions. This suggests that the error in the predictions may result from experimental error rather than from lack of fit of the model. However, further experimentation and statistical analysis of the model are needed to confirm the applicability of the model. For compounds such as p-xylene which are primarily removed by biodegradation, the results suggest that the model can give reasonably good predictions. For the chlorinated compounds which are both stripped and possibly biodegraded to a substantial extent, the predictions are less accurate.

In fitting the biodegradation rate constants and Henry's law coefficients, no attempt was made to discard apparent outliers in the data. Attempting to fit these extreme values may tend to distort the fitted parameters and thus cause the scatter in the predictions. It is likely that better correspondence between observed and predicted values could be obtained if some of the experiments were discarded. If this were to be done, a sound statistical basis for determining which experiments to discard should be used.

A temperature correction was used in fitting the biodegradation rate constants. No temperature correction was used in fitting the Henry's law coefficients. The current model does not include temperature correction of the biodegradation rate constants or the Henry's law coefficients. Incorporation of temperature correction into the model and the parameter fitting may result in improved model predictions.

### 4.2.2 U.S. EPA Pilot Plant

The steady state model was tested against data from the U.S. EPA pilot plant program (Govind et al., 1989). The pilot plant design and operating parameters are given in Table 4.10. Results of the model tests are given in Tables 4.11 - 4.13. Table 4.11 gives the observed and predicted percent removals by volatilization and sorption in the primary clarifier. Table 4.12 gives the observed and predicted percent removals by stripping and sorption in the aeration basin. In this case the stripping removals are the sum of stripping and surface volatilization. Table 4.13 gives the observed and predicted removals by biodegradation in the aeration basin and the total plant removals.

Table 4.10 EPA Pilot Plant Design and Operating Parameters

| | |
|---|---|
| Primary Clarifier Surface Area ($m^3$) | 6.8 |
| Primary Clarifier Depth (m) | 3.7 |
| Secondary Clarifier Surface Area ($m^3$) | 10.4 |
| Secondary Clarifier Depth (m) | 3.7 |
| Aeration Basin Volume ($m^3$) | 59.7 |
| Aeration Basin Depth (m) | 3.7 |
| Aeration Basin Hydraulics | 1 CSTR |
| Type of Aeration | Subsurface |
| Air Flow Rate ($m^3$/h) | 324.6 |
| Oxygen Transfer Efficiency (%) | 4 |
| Dissolved Oxygen Concentration (mg/L) | 2.0 |
| MLVSS Concentration (g/L) | 2.0 |
| Wastewater Temperature (°C) | 25 |
| Wastewater Flow Rate ($m^3$/h) | 7.95 |
| Secondary Sludge Wasting Rate ($m^3$/d) | 4.1 |
| Sludge Recycle Ratio (%) | 46.4 |
| Influent Suspended Solids Conc. (mg/L) | 67.5 |
| Suspended Solids Removal in Primary (%) | 50 |
| Wind Speed (m/s) | 0.03 |

Table 4.11 EPA Pilot Plant Modelling - Primary Clarifier

| | Observed | | Predicted | |
|---|---|---|---|---|
| Compound | % Volatil. | % Sorbed | % Volatil. | % Sorbed |
| Chloroform | 8.1 | 0.6 | 0.3 | 0.4 |
| Dichloromethane | 7.9 | 1.2 | 0.3 | 0.2 |
| Tetrachloroethylene | 9.4 | 0.2 | 0.3 | 1.5 |
| Trichloroethylene | 10.1 | 0.9 | 0.3 | 1.0 |
| 1,1,1-Trichloroethane | 10.6 | 0.6 | 0.3 | 0.9 |
| Ethylbenzene | 9.6 | 0.8 | 0.3 | 2.2 |
| Toluene | 9.8 | 0.6 | 0.3 | 1.2 |
| Xylenes | 9.8 | 0.8 | 0.3 | 2.2 |
| 1,4- Dichlorobenzene | 0.0 | 1.7 | 0.3 | 3.0 |

Table 4.12 EPA Pilot Plant Modelling - Aeration Basin

| Compound | Observed<br>% Stripped | <br>% Sorbed | Predicted<br>% Stripped | <br>% Sorbed |
|---|---|---|---|---|
| Chloroform | 109.4 | 0.11 | 32.4 | 0.57 |
| Dichloromethane | 77.9 | 0.00 | 32.8 | 0.13 |
| Tetrachloroethylene | 157.0 | 0.40 | 53.4 | 0.56 |
| Trichloroethylene | 128.4 | 0.01 | 50.6 | 0.34 |
| 1,1,1-Trichloroethane | 137.6 | 0.03 | 40.8 | 0.25 |
| Ethylbenzene | 20.7 | 0.01 | 5.2 | 0.07 |
| Toluene | 28.3 | 0.05 | 5.2 | 0.04 |
| Xylenes | 39.7 | 0.01 | 8.1 | 0.09 |
| 1,4- Dichlorobenzene | 0.0 | 0.02 | 66.1 | 2.98 |

Table 4.13 EPA Pilot Plant - Aeration Basin & Total Plant Removal

| Compound | Observed<br>% Biodeg. | <br>% Total | Predicted<br>% Biodeg. | <br>% Total |
|---|---|---|---|---|
| Chloroform | 0.0 | 84.1 | 40.9 | 74.7 |
| Dichloromethane | 0.0 | 73.3 | 51.2 | 84.7 |
| Tetrachloroethylene | 0.0 | 95.2 | 37.3 | 93.1 |
| Trichloroethylene | 0.0 | 82.6 | 41.0 | 93.2 |
| 1,1,1-Trichloroethane | 0.0 | 97.9 | 52.4 | 94.6 |
| Ethylbenzene | 67.5 | 98.7 | 91.6 | 99.4 |
| Toluene | 60.1 | 98.9 | 92.7 | 99.4 |
| Xylenes | 48.4 | 98.7 | 88.5 | 99.2 |
| 1,4- Dichlorobenzene | 93.0 | 94.7 | 9.1 | 81.7 |

In general, the model predicted less volatilization in the primary clarifier than observed. Since volatilization is dependent on wind speed, the wind speed estimate used in the model may have been too low. The wind speed was estimated from the air flow data given by Govind et al. (1989). The actual primary clarifier was covered and an artificial wind was created to sweep the surface. Additional information not available in the reference may be needed to determine the appropriate wind speed to model.

The model predicted slightly higher sorption removal in the primary clarifier than observed for seven of nine compounds. For most of the compounds the observed and predicted values are of the same order of magnitude. Since only minimal plant operational data are available in the reference, the predictions may be able to be improved with additional plant operational information.

In general, the model predicted less stripping in the aeration basin than observed. For four of the nine compounds the observed percent removal by stripping was greater than 100% suggesting error in the off-gas or liquid measurements. Except for 1,4-dichlorobenzene, the relationship of the percent removals between compounds was roughly the same for observed and predicted results. No stripping of 1,4-dichlorobenzene was observed while the model predicted substantial removal by stripping. Substantial stripping of 1,4-dichlorobenzene was observed in the WTC pilot plant.

Generally, the observed and predicted total plant removals corresponded reasonably well, particularly for the three non-chlorinated aromatic compounds. The total plant removals are based only on influent and effluent wastewater analysis. Off-gas and waste sludge concentrations were not used to compute total removals.

### 4.2.3 Highland Creek WPCP

Data from the Highland Creek WPCP (Thompson et al., 1989) were compared to steady state model predictions. The Highland Creek plant is a municipal activated sludge plant with a relatively heavy input of VOCs. The plant design and operating parameters are given in Table 4.14. Tables 4.15 and 4.16 summarize the observed and predicted percent removals by stripping and biodegradation in the aeration basin. Table 4.17 gives the observed and predicted overall removals in the aeration basin. Biodegradation removals were computed by mass balance difference assuming negligible removal by sorption.

Table 4.14 Highland Creek WPCP Design and Operating Parameters

| | |
|---|---|
| Aeration Basin Volume ($m^3$) | 23,168 |
| Aeration Basin Depth (m) | 4.6 |
| Aeration Basin Hydraulics | 1 CSTR |
| Type of Aeration | Subsurface |
| Air Flow Rate ($m^3$/h) | 14,304 |
| Oxygen Transfer Efficiency (%) | 9 |
| Dissolved Oxygen Concentration (mg/L) | 2.9 |
| MLVSS Concentration (g/L) | 3.4 |
| Wastewater Temperature ($^oC$) | 20 |
| Wastewater Flow Rate ($m^3$/h) | 3263 |
| Secondary Sludge Wasting Rate ($m^3$/d) | 530 |
| Sludge Recycle Ratio (%) | 37 |
| Wind Speed (m/s) | 0 |

Table 4.15 Highland Creek WPCP Modelling - Stripping

| | | % Stripped | | | |
|---|---|---|---|---|---|
| | | Observed | | * | |
| Compound | Exp.1 | Exp.2 | Exp.3 | Average | Predicted |
| Dichloromethane | 3.2 | 1.7 | 2.8 | 2.6 | 3.5 |
| Chloroform | 6.1 | 8.2 | 7.8 | 7.4 | 3.6 |
| 1,1,1-Trichloroethane | 8.5 | 13.6 | 9.4 | 10.5 | 5.3 |
| Trichloroethylene | 7.0 | 9.8 | 15.3 | 10.7 | 7.6 |
| Toluene | 0.5 | 1.5 | 1.7 | 1.2 | 0.4 |
| Tetrachloroethylene | 60.9 | 77.0 | 38.3 | 58.7 | 8.9 |
| p-Xylene | 0.3 | 1.6 | 2.0 | 1.3 | 0.9 |
| 1,4-Dichlorobenzene | 14.4 | 20.1 | 22.8 | 19.1 | 17.0 |

Table 4.16 Highland Creek WPCP Modelling - Biodegradation

| | | % Biodegraded | | | |
|---|---|---|---|---|---|
| | | Observed | | * | |
| Compound | Exp.1 | Exp.2 | Exp.3 | Average | Predicted |
| Dichloromethane | 89.9 | 96.2 | 91.2 | 92.4 | 81.2 |
| Chloroform | 75.4 | 68.7 | 76.8 | 73.6 | 69.2 |
| 1,1,1-Trichloroethane | 80.4 | 76.9 | 81.9 | 79.7 | 88.8 |
| Trichloroethylene | 83.9 | 87.3 | 77.0 | 82.7 | 83.4 |
| Toluene | 99.4 | 98.4 | 98.1 | 98.6 | 99.1 |
| Tetrachloroethylene | 24.8 | -27.0 | 49.7 | 15.8 | 81.1 |
| p-Xylene | 99.5 | 97.4 | 97.4 | 98.1 | 98.6 |
| 1,4-Dichlorobenzene | 60.6 | 54.3 | 49.3 | 54.7 | 34.6 |

Table 4.17 Highland Creek WPCP Modelling - Overall Removal

| | | % Removed | | | |
|---|---|---|---|---|---|
| | | Observed | | * | |
| Compound | Exp.1 | Exp.2 | Exp.3 | Average | Predicted |
| Dichloromethane | 93.1 | 97.9 | 94.0 | 95.0 | 84.8 |
| Chloroform | 81.5 | 76.9 | 84.6 | 81.0 | 73.3 |
| 1,1,1-Trichloroethane | 88.9 | 90.5 | 91.3 | 90.2 | 94.2 |
| Trichloroethylene | >90.9 | 97.1 | >92.3 | >93.4 | 91.4 |
| Toluene | >99.9 | 99.9 | >99.8 | >99.9 | 99.6 |
| Tetrachloroethylene | 85.7 | 50.0 | 88.0 | 74.6 | 90.5 |
| p-Xylene | >99.8 | >99.0 | >99.4 | >99.4 | 99.5 |
| 1,4-Dichlorobenzene | 75.0 | 74.4 | 72.1 | 73.8 | 56.4 |

The predicted removals by stripping and biodegradation corresponded reasonably well with the observed values except for tetrachloroethylene. For tetrachloroethylene, the model underestimated stripping and overestimated biodegradation. The data for tetrachloroethylene for both the WTC pilot plant and the Highland Creek plant exhibited more scatter than the other compounds. This may have caused an inaccurate fit of the Henry's law coefficient and the biodegradation rate constant, resulting in poor model predictions. Experiment 2 had an influent tetrachloroethylene concentration near the detection limit, possibly resulting in error in the data. The mass balance for Experiment 2 resulted in a negative percent biodegradation. If Experiment 2 was discarded, the correspondence between observed and predicted removals was somewhat improved. However, the model still underestimated stripping and overestimated biodegradation, but the predicted overall removal was reasonably close to the observed value.

The model appeared to underestimate biodegradation of 1,4-dichlorobenzene but predicted stripping reasonably well. As noted in section 3.3, the 1,4-dichlorobenzene biodegradation rate constant obtained from the WTC pilot plant data was substantially less than that obtained from the EPA pilot plant data.

In general, the model predictions were reasonably close to the observed values, suggesting that a model of the current form may be able to provide reasonably accurate predictions of full scale plant performance when calibrated with pilot plant data. Further work appears to be needed to refine the treatability parameters, particularly for the chlorinated compounds.

### 4.2.4 Petroleum Refineries

Steady state model predictions were compared with observed VOC removals in three petroleum refinery wastewater treatment plants. Data for the Esso Refinery in Sarnia, Ontario and the Petro-Canada Refinery in Oakville, Ontario were obtained from Canviro Consultants (1987). Additional data for the Petro-Canada Refinery were obtained from Environment Canada (1988). Data for the Montreal East Refinery were obtained from IEC Beak Consultants (1985). Except for the Environment Canada (1988) study, no data were available for VOC stripping. The air stripping data from the Environment Canada (1988) study were not usable for model testing because the mass balances showed much greater quantities of VOCs emitted to the air than entered in the influent. Therefore, only the overall percent removals were compared.

Table 4.18 gives the design and operating parameters for the three refinery treatment plants. Tables 4.19 - 4.21 give the observed and predicted percent removals in the activated sludge systems at the three plants.

Table 4.18 Refinery Plant Design and Operating Parameters

| | Esso | Petro-Canada | Montreal East |
|---|---|---|---|
| Primary Clarifier Surface Area ($m^3$) | NA | NA | 948 |
| Primary Clarifier Depth (m) | NA | NA | 8.5 |
| Secondary Clarifier Surface Area ($m^3$) | 1784 | 118 | 690 |
| Secondary Clarifier Depth (m) | 3 | 3 | 4 |
| Aeration Basin Volume ($m^3$) | 5472 | 1336 | 10,555 |
| Aeration Basin Depth (m) | 5 | 5 | 5 |
| Aeration Basin Hydraulics | 1 CSTR | 3 CSTRs | 1 CSTR |
| Type of Aeration | Surf. | Sub. | Sub. |
| Total Aerator Power (kW) | 100 | NA | NA |
| Standard Oxygen Transfer Rate (kg/h/kW) | 1.8 | NA | NA |
| Aerator Power Delivery Efficiency (%) | 80 | NA | NA |
| Dirty $H_2O$/Clean $H_2O$ Correction Factor | 0.8 | NA | NA |
| Air Flow Rate ($m^3$/h) | NA | 3700 | 11,850 |
| Oxygen Transfer Efficiency (%) | NA | 4 | 4 |
| Dissolved Oxygen Concentration (mg/L) | NA | 1.1 | 2.0 |
| MLVSS Concentration (g/L) | 4.8 | 1.2 | 1.1 |
| Wastewater Temperature ($^{\circ}$C) | 32 | 36 | 20 |
| Wastewater Flow Rate ($m^3$/h) | 971.6 | 207.0 | 703.0 |
| Secondary Sludge Wasting Rate ($m^3$/d) | 44.8 | 1.5 | 189 |
| Sludge Recycle Ratio (%) | 106 | 134 | 28 |
| Wind Speed (m/s) | 0 | 0 | 2.5 |

Table 4.19 Esso Refinery Modelling

| Compound | Observed % Removal | Predicted % Removal |
|---|---|---|
| Benzene | >98.7 | 99.7 |
| Toluene | >98.1 | 99.7 |
| Xylenes | >99.6 | 99.5 |
| Ethylbenzene | >97.6 | 99.7 |

Table 4.20 Petro-Canada Refinery Modelling

| Compound | Observed % Removal[1] | Observed % Removal[2] | Predicted % Removal |
|---|---|---|---|
| Benzene | >99.9 | 82.5* | 99.97 |
| Toluene | >99.9 | 97.4** | 99.96 |
| Xylenes | >99.9 | 95.8*** | 99.87 |
| Ethylbenzene | >99.2 | ---- | 99.93 |

* 64% of samples had 100% removal
** 79% of samples had 100% removal
*** 92% of samples had 100% removal

[1] Canviro Consultants (1987)
[2] Environment Canada (1988)

Table 4.21 Montreal East Refinery Modelling

| Compound | Observed % Removal | Predicted % Removal |
|---|---|---|
| Benzene | 99.6 | 99.4 |
| Toluene | 99.4 | 99.4 |
| Xylenes | 98.4 | 99.2 |

For all three refinery treatment plants, the observed and predicted overall removals corresponded well. All of the compounds compared in the refinery data were non-chlorinated aromatic compounds which were nearly 100% removed in the treatment processes.

## 4.3 Dynamic Model

The dynamic model was tested against data from the Galt WPCP. The design and operating parameters for the Galt treatment plant are given in Table 4.22. Test results are shown graphically on Figures 4.1 - 4.3 for the three chlorinated VOCs tested.

Table 4.22 Galt WPCP Design and Operating Parameters

| | |
|---|---|
| Grit Chamber Surface Area ($m^3$) | 100 |
| Grit Chamber Depth (m) | 3 |
| Primary Clarifier Surface Area ($m^3$) | 1050 |
| Primary Clarifier Depth (m) | 2.9 |
| Secondary Clarifier Surface Area ($m^3$) | 1650 |
| Secondary Clarifier Depth (m) | 3 |
| Aeration Basin Volume ($m^3$) | 6600 |
| Aeration Basin Depth (m) | 4.2 |
| Aeration Basin Hydraulics | 1 CSTR |
| Type of Aeration | Surface |
| Total Aerator Power (kW) | 117.6 |
| Standard Oxygen Transfer Rate (kg/h/kW) | 1.8 |
| Aerator Power Delivery Efficiency (%) | 80 |
| Dirty $H_2O$/Clean $H_2O$ Correction Factor | 0.8 |
| MLVSS Concentration (g/L) | 1.04 |
| Wastewater Temperature (°C) | 15 |
| Wastewater Flow Rate ($m^3/h$) | 1288 |
| Secondary Sludge Wasting Rate ($m^3/d$) | 717 |
| Sludge Recycle Ratio (%) | 78 |
| Influent Suspended Solids Conc. (mg/L) | 102 |
| Suspended Solids Removal in Primary (%) | 50 |
| Wind Speed (m/s) | 1.0 |

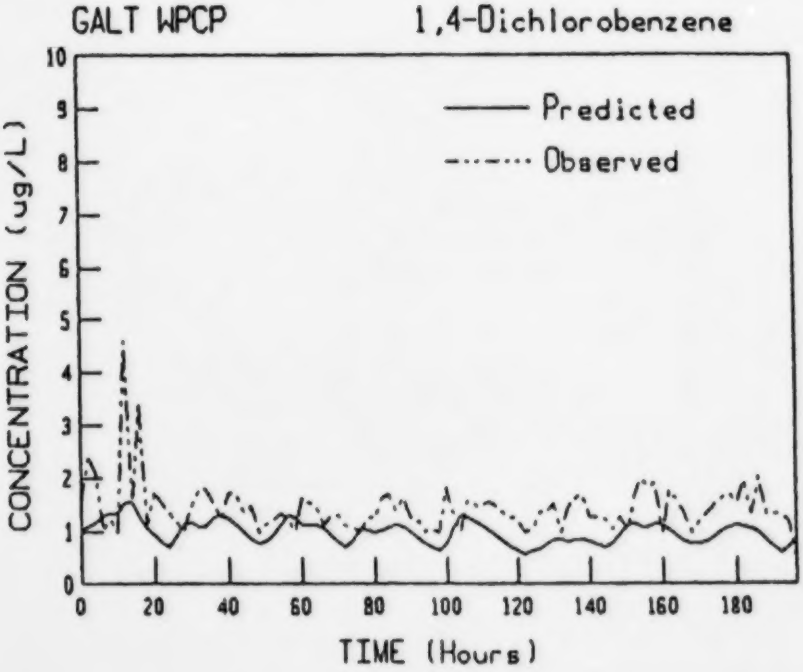


Figure 4.1 Dynamic Model Test Results - 1,4-Dichlorobenzene

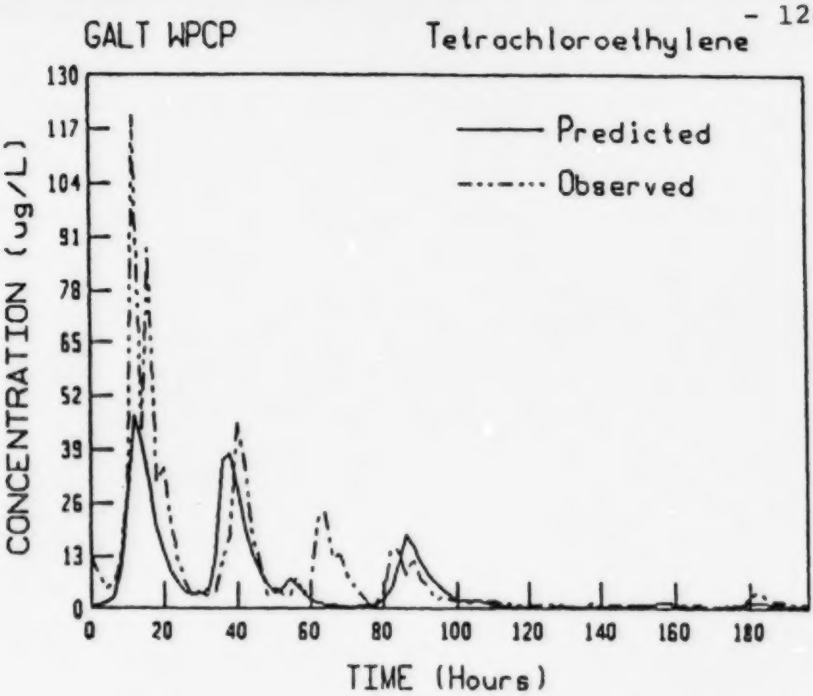


Figure 4.2 Dynamic Model Test Results - Tetrachloroethylene

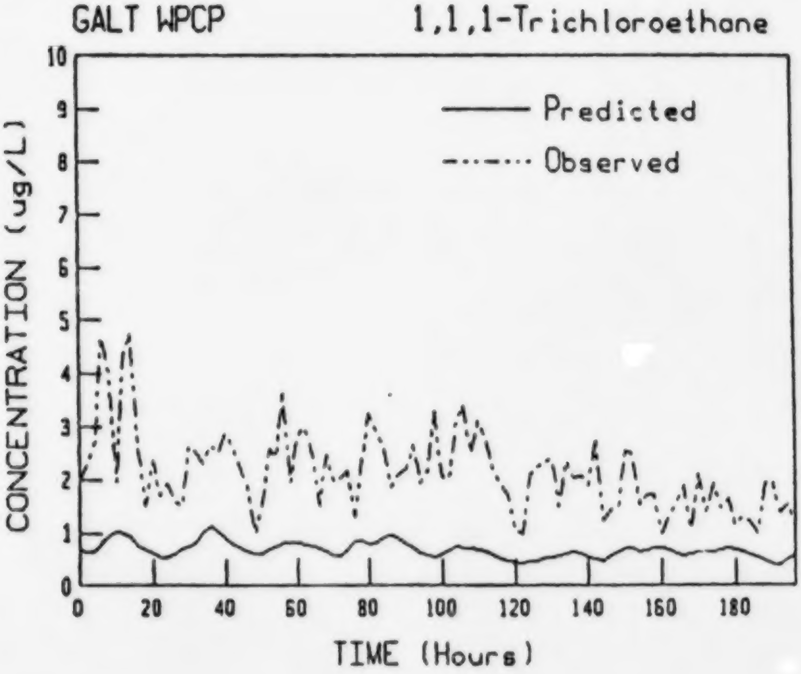


Figure 4.3 Dynamic Model Test Results - 1,1,1-Trichloroethane

For 1,4-dichlorobenzene, the model appeared to slightly overestimate the overall removal by the treatment plant. However, the model predictions appeared to follow the trend of the observed effluent concentrations reasonably well. This suggests that the current form of the model may provide reasonable dynamic predictions with improved calibration.

The model predictions for tetrachloroethylene also appeared to generally follow the trend of the observed effluent concentrations. The magnitude of the peak concentrations observed near the beginning of the sampling period were underestimated by the model. However, at the beginning of the sampling period the effluent concentrations may have been affected by influent concentrations which occured before the start of the sampling period, and were therefore unknown.

The predicted effluent concentrations for 1,1,1-trichloroethane were consistently less than the observed concentrations suggesting a lack of calibration of the model for this compound. The predicted concentrations generally followed the trend of the observed concentrations, however. Some error may also have resulted from inaccurate estimates of plant operating parameters where complete information was not available in the reference source.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The following are the conclusions and recommendations resulting from tests of the computer based steady state and dynamic models for predicting the fate of contaminants in wastewater treatment plants:

1. The steady state and dynamic models in their present form appear able to give reasonable predictions of the fate of VOCs in municipal and industrial activated sludge wastewater treatment plants provided they are properly calibrated.

2. The steady state model produced more accurate predictions for highly biodegraded non-chlorinated aromatic compounds than for chlorinated hydrocarbons.

3. The effluent concentration predictions of the dynamic model appeared to follow the trend of the observed concentrations, although the accuracy of the predictions requires improvement.

4. The test results suggest that treatability parameters developed in pilot plant tests can be used to predict the performance of full scale plants.

5. Additional testing should be carried out on other classes of hazardous compounds to determine the applicability of the model for a wider range of contaminants.

6. The treatability parameter data base should be expanded by carrying out additional pilot plant and bench scale tests.

7. Temperature correction should be incorporated into the model and the parameter fitting for biodegradation, volatilization, and stripping.

8. More sophisticated statisical methods for treatability parameter fitting should be investigated to improve model calibration.

9. Additional full scale plant testing of the models should be carried out to confirm the applicability of the models.

10. Additional mathematical models for the different removal mechanisms should be investigated to determine whether the model predictions can be improved.

## 6. REFERENCES

Canviro Consultants, "Sampling and Analysis of Refinery Effluents to Assess Variations in Trace Contaminants Concentrations", Petroleum Association for Conservation of the Canadian Environment (PACE), Ottawa, Ontario (1987).

Canviro Consultants, "Fluctuations of the Trace Contaminants in Municipal Sewage Treatment Plants, Phase II Field Studies", Project KI23431.AO, Waterloo, Ontario (1988).

Dobbs, R.A. et al., "Partitioning of Toxic Organic Compounds on Municipal Wastewater Treatment Plant Sludges", Proceedings of the International Conference on Innovative Biological Treatment of Toxic Wastewaters, Arlington, Virginia (1986).

Environment Canada, "The Petrocanada Volatilization Study", Draft Report, Environment Canada, Pollution Abatement Division, Toronto, Ontario (1988).

Govind, R. et al., "Effect of Abiotic Mechanism on the Fate of Compounds in a Wastewater Treatment Plant", Presented at the Hazardous Waste Treatment: Biosystems for Pollution Control Symposium, Cincinnati, Ohio (1989).

IEC Beak Consultants Ltd., "Fate and Transformation of Selected Trace Organics in Refinery Wastewater Treatment", Petroleum Association for Conservation of the Canadian Environment (PACE), Report No. 85-7, Ottawa, Ontario (1985).

Mackay, D. and Yeun, T.K., "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water", Environ. Sci. Technol., **17**, 211 (1983).

Matter-Muller, C. et al., "Transfer of Volatile Substances from Water to the Atmosphere", Water Res., **15**, 1271 (1981).

Munz, C. and Roberts, P.V., "The Ratio of Gas-Phase Mass Transfer Coefficients in Gas-Liquid Contacting Processes", in Gas Transfer at Water Surfaces, W. Brutsaert and G.H. Jirka (eds.), D. Reidel Publishing Company (1984).

Thibodeaux, L.J., Chemodynamics, John Wiley and Sons, New York (1979).

Thompson, D. et al., "Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems, Phase II", Ontario Ministry of the Environment, Toronto, Ontario (1989).

PCAO SYMPOSIUM : NOVEMBER 23, 1989
"FATE OF CHEMICALS IN SEWAGE TREATEMENT FACILITIES"

# OCCUPATIONAL ASSESSMENT OF EXPOSURE TO CHEMICALS AT METROPOLITAN TORONTO SEWAGE TREATMENT PLANTS

KIRBY JAMES, BSc, MHSc, IHIT
CORPORATE OCCUPATIONAL HYGIENIST, CORPORATE HEALTH AND SAFETY
MUNICIPALITY OF METROPOLITAN TORONTO
7 KING ST. EAST, TORONTO

## INTRODUCTION

Over the course of 1988 and 1989 the Municipality of Metro Toronto undertook a major project to evaluate the exposure of Sewage Treatment Plant (STP) workers to hazardous chemicals. What made this particular chemical exposure assessment unique was that rather than taking the usual compliance monitoring approach Metro went on to develop a computer model that would predict the total body exposure of an STP worker. To predict total body exposure results from chemical analyses of solid, liquid and airborne materials were combined with day to day work practices variables such as level of physical effort and personal hygiene practices.

Furthermore, the contracted toxicology consulting firm (ECO LOGIC) assisted Metro in making this a joint labour - management project by facilitating the project from definition of project scope through acceptance of the computer model findings.

At the conclusion of our efforts major strides were made to identify not just the toxic chemicals of concern, but also the individual routes of toxic chemical entry into the body and predicted amounts that workers were encountering on the job. Notably this project identified no chemicals of concern using the conventional approach of exposure assessments but up to six significant chemicals of concern using our predictive model. Armed with such information modifications to procedures and training have resulted to reduce the risks of chemical exposure in the STP work place environment.

Special mention is deserved of the vision displayed by Mr. Mike Thorne, Director of the Water Pollution Control Division to see this project through from conceptualization to completion. Technical direction was provided from the Occupational Hygiene section of

Corporate Health and Safety and tremendous cooperation was offered by staff at each STP operation.

## PROJECT BACKGROUND

As the theme of this symposium has outlined, hazardous chemicals have become integrated into the municipal waste stream our sewage treatment facilities process. As the Minister of the Environment, Jim Bradley, has stated one important reason for reducing industrial waste dumping to the sewer system is the danger such materials represent to STP workers. In particular it is the uncontrollable combination of various toxic chemicals and their resulting by-products that are of concern.

A conventional occupational exposure assessment approach would measure the chemical exposure of a worker using equipment and science developed by the field of Industrial Hygiene, or as it is known in Canada, Occupational Hygiene. A sample is taken of the air a worker is breathing for a specific chemical or chemicals by collecting a sample of air on an appropriate sampling medium. Samples were then analyzed in the lab to provide an amount of chemical detected and calculate an airborne chemical concentration using the air sample volume. This concentration is then averaged over a work day to provide a standard unit of measure for comparison to governmental standards. At present this constitutes the fundamental North American airborne chemical hazard evaluation. Note that the only medium assessed by this standard practice is the **air**.

A major concern of workers in the four Metro Toronto treatment plants was that these standards were designed for workers who primarily encountered limited numbers of known airborne chemicals. It was stated by Joint Health and Safety committee representatives that their environment contained variable, unknown chemical hazards that fell outside of the existing framework for determining a safe work place. In particular the nature of many STP tasks requires dermal or skin contact with chemically contaminated sewage by-products, for example during pump repair. What effect did this have on workers and how could overexposure be assessed due to dermal contact? Were there other significant routes of exposure?

Technologically the STP air environment makes conventional air sampling for gases and vapours difficult because of high moisture levels. Standard practice for measuring volatile and semi-volatile compounds is to use activated charcoal sampling media that is usually analyzed for a restricted number of chemical compounds. Unfortunately high humidity causes interferences with activated charcoal and therefore reliable results are difficult to achieve in this environment.

It became clear that for the sewage treatment plant environment an occupational exposure assessment should be of broader scope than the conventional approach while still satisfying the usual air monitoring requirements. With this objective a strategy to satisfy these concerns were developed.

## PROJECT APPROACH

Based on worker concerns and available air monitoring data it became clear that technical hurdles had to be overcome to not only produce reliable air monitoring results but also address the concerns of total body exposure. To accomplish these concerns the three major project components were addressed:

a) air monitoring technical hurdles;
b) labour-management collaboration to identify and address chemical exposure concerns; and
c) development of an acceptable and valid predictive computer model for total body exposure.

To resolve the problem of reliable results in a high humidity environment with numerous chemicals Tenax GC adsorbent was selected as the sampling media because of its hydrophobicity and good retention efficiency of volatile and semi-volatile chemicals. For analysis GC-MS, that is Gas Chromatography - Mass Spectrophotometry, was used to identify all collected compounds by both molecular mass and ion structure. To provide reliability on the data, every single sample was laboratory spiked with surrogate compounds containing bromine to permit a thorough Quality Assurance/Quality Control program.

By using Tenax GC sampling media and GC-MS analytical technology the scope of the chemical assessment in air was expanded from a typical 4 to 10 compounds per sample up to 78 target compounds. Included in the target chemical group were the PCB isomers, several common pesticides and many chlorinated and sulphonated organics.

To address the question of exposure to sludges, effluents and process flow materials throughout the plants samples were collected at numerous stages in the process flow. These materials were then analyzed using GC-MS technology for the same target compounds. Ashes were analyzed for additional materials including heavy metals and dioxins.

Information was compiled on the chemical composition of the air, solids and liquids throughout our four STP's over a four month time frame with over 70 samples of the various media collected. Samples were collected instantaneously, over 12 hour and 24 hour periods. Composite sludge and ash samples were taken and averaged for different sample periods.

To enhance the acceptance of not only the results but the process of taking a new approach to total body exposure, this project was conducted as a joint labour-management effort. Meetings were regularly held over the project and collective input was used to direct the timing and location of sample collection. With this approach it was believed that treatment plant workers would be the best source of information for identifying areas of concern.

Armed with reliable and reproducible results of the concentrations of chemicals in the various media, development began of a computer based model to predict worker total body exposure. Research was conducted by ECO LOGIC toxicologists and Metro Hygiene staff to provide information that would account for variations in exposures. In summary the elements that were focused upon in the computer model were the primary routes of entry or exposure:

a) inhalation;
b) dermal exposure; and
c) accidental ingestion.

## COMPUTER MODEL COMPONENTS

The computer model would go on to integrate the data collected from air, sludge, ash and effluent analyses into a single number representative of worker exposure. To provide this single value the exposures from the three routes of entry were individually modelled and then combined for a total body exposure level. The total daily exposure was expressed as milligrams of chemical per shift.

## Inhalation Model

Breathing rates and volumes depend on your level of effort. If an STP operator is sitting down or slowly walking around the plant that persons' breathing rate will be substantially lower than for a maintenance worker engaged in moderate physical labour. The duration of exposure also affects the total volume of air a person breathes at work. Finally, if the worker wears a respirator the amount of chemical that can be inhaled is affected. All of these elements are specified when using the program to account for variable levels of effort and work conditions. Individual data entry on chemical concentrations in air are combined with these variables.

By using a computer model approach an advantage was gained over existing conventional exposure tests to account for variations in effort at work and therefore inhalation of more chemicals in air. As a predictive tool this approach would be expected to show that maintenance workers exerting themselves vigorously would encounter more chemical exposure than an operator in the same area who was engaged in less physical activity based on the larger volume of air inhaled.

## Dermal Model

To address exposure due to skin contact with chemically contaminated sewage sludge, a model was developed to account for the following variables:

a) amount of body surface area exposed, ie. in contact with contaminated material;
b) concentration of chemicals in sewage sludge; and
c) percentage of chemicals in sludge or ash available for skin absorption.

The availability of chemicals in sludges and ashes, particularly heavy metals was determined by laboratory tests using simulated sweat solution to evaluate chemical leachability. Once the leachable percentage was determined the availability for absorption through the skin was estimated from known scientific references.

With this modelling approach a prediction became possible to illustrate that in certain cases, for example when chemical concentrations in air are low, it is still possible to experience significant chemical exposure due to skin exposure.

### Ingestion Model

The factor which primarily affects accidental ingestion of contaminated sludge in the work place is personal hygiene practices. Like the dermal model, the evaluation of ingestion exposure provides for input on the concentration of chemicals in sludge or ash, but additionally accounts for whether a worker washes their hands before eating/drinking/smoking and if in fact the worker smokes on the job. Using research information on the amount of material children accidentally ingest as a reference point a prediction of exposure was made to provide a daily estimate of ingestion exposure for workers in this study.

With this ingestion another existing route of exposure was quantified and summed with both inhalation and dermal exposure as milligrams of chemical per shift.

### Acceptable Daily Intake

In order to compare the total body exposure output of this computer model, expressed in milligrams of chemical per shift, an exposure guideline of similar kind was required. Reference was made to existing regulated exposures limits for chemicals in air and where unavailable World Health Organization Drinking Water guidelines and these values were modified for comparison to the total body exposure. These guideline levels are referred to as Acceptable Daily Intakes (ADI's).

Where a standard existed for a chemical, for example total PCB's, the value listed by the Ministry of Labour was converted from an average concentration over 8 hours to an actual amount of PCB's the worker would be permitted to inhale under the regulated limits. To effect this conversion the government air concentration standard in milligrams per cubic meter (mg/m3) was multiplied by the minimum expected air volume a worker would inhale over an 8 hour shift, 3.34 cubic meters as determined through reference texts. This would convert the M.O.L. standard for PCB's of 0.05 mg/m3 to 0.16 milligrams of PCB's per shift total body exposure. As the M.O.L. Time Weighted Average Exposure Value (TWAEV) has been created to protect the majority of workers from illness, by converting the air concentration standard to an acceptable total body exposure it becomes possible to include the contribution of dermal and ingestion exposure.

World Health Organization drinking water guidelines were converted to ADI's by multiplying the acceptable concentration by the normal fluid intake of a 70 kilogram male on a daily basis.

This reference point is a useful tool, but one which does not entirely account for the differences in the absorption of chemicals through different tissues. With this limitation in mind it permits the inclusion of two highly significant routes of entry when evaluating the full picture of worker exposure.

### Mixed Toxicity Calculations

As required by M.O.L. regulations, an evaluation was also made of the effects of exposure to multiple chemicals with similar toxic effects. The conventional method of multiple exposure evaluation is to sum the measured exposure divided by its appropriate standard.

[PCB's in air / PCB standard] + [carbon tetrachloride in air/ carbon tetrachloride standard]

If this value exceeds 1 then a worker is overexposed. For the purposes of comparing total body exposure this same approach was used with the ADI's as a reference guideline. As a conservative measure, when the total body multiple exposure value was more than 0.75 a worker was considered overexposed.

## PROJECT FINDINGS

### Conventional Approach

With a total of 78 air samples for 75 chemicals, plus sludge and ash analyses for the same scope of chemicals a total of 6500 data points were obtained.

Of all the air sampling records only two out of 5850 results, or 0.03%, were above existing M.O.L. standards and in unpopulated, inaccessible plant areas. This project did not, however, evaluate the typical lighter products of methane and hydrogen sulphide.

Had Metro pursued the exposure evaluation project to this point the findings would have been similar to those found throughout the literature, that is that exposure to chemicals in sewage treatment plants are typically not a major concern. Exceptions to this are when an industrial discharge of large size containing volatile or reactive material enters the system usually in close proximity to the plant.

At the project outset workers expressed concerns with short term "slugs" of chemicals but existing procedures and equipment document these hazards. Of more importance were the career long implications of simultaneous exposure to numerous low levels of chemicals in the air and process materials. In conclusion the conventional assessment findings did not indicate any notable concern with the work place environment.

## Computer Model Approach

To differentiate between work force populations two "worker conditions" were established: Operator and Maintenance Worker. The operator works at an easier pace, comes into less skin contact with process materials, works a 12 hour shift and does not frequently wear a respirator. Maintenance workers often work at moderate physical levels, come into "intimate" physical contact with various process materials, work an 8 hour shift and often wear respirators.

These work practice variables were combined with the chemical concentrations of sludge, air, ash and effluent or plant water to calculate a total daily exposure.

Without exception two trends were observed. First, more chemicals of concern were detected using the computer model as compared to the conventional exposure assessment approach. Secondly, maintenance workers were predicted to be exposed to more chemicals at higher concentrations than operators.

Significant findings were made for chemicals of concern not detected by the conventional approach. Of primary concern were:

a) hexachlorobenzene; and
b) heavy metals.

Hexachlorobenzene is a confusing finding as the MISA project did not identify this compound as a concern. Our hypothesis is that this material, present in very low concentrations but of very high toxicity, may be either peculiar to Metro at the point in time of the study or is a process by-product.

Heavy metals are a known concern, but through the computer model the degree of exposure was greater than anticipated. Of primary importance were chromium, cadmium and lead.

The identification of maintenance workers as a work force population at higher exposure was not surprising. The routes of entry did provide a change to our perception of chemical exposure as dermal absorption and accidental ingestion accounted for the majority of exposure, **not air exposure levels**.

## CONCLUSION

In summary, by using a toxicological approach to supplement the traditional Occupational Hygiene exposure assessment strategy Metro was able to provide insight into a complex work environment. The conventional sampling requirements were addressed only to be implicated as insufficient in the Sewage Treatment Plant work environment. While the computer model and underlying assumptions are in the process of peer review, fundamentals of Occupational Hygiene, exposure standard formulation and toxicology were applied to arrive at the final product.

This project has received widespread interest and within Metro, is viewed as a progressive step to providing a safer work place. It is particularly significant that the major routes of chemical exposure, that is skin absorption and accidental ingestion, can be addressed by protective measures that also reduce the long known risks of infection by biological agents.

# SURVEY OF ONTARIO MUNICIPAL TREATMENT PLANT EFFLUENT TOXICITY

Presentation at PCAO/MOE Seminar on
Fate of Chemicals in Sewage Treatment Facilities

London, Ontario

November 23, 1989

Hugh Monteith
Ministry of the Environment
MISA Municipal Section
Water Resources Branch

# SURVEY OF ONTARIO MUNICIPAL TREATMENT PLANT EFFLUENT TOXICITY

## 1.0 INTRODUCTION

### 1.1 Overview

In the Municipal-Industrial Strategy for Abatement (MISA) Program, the Ontario Ministry of the Environment (MOE) will restrict the discharge of toxicants from nine industrial categories and from municipal sewage treatment plants (STPs).

Under MISA, Regulations will be promulgated which will require monitoring and compliance with limits on conventional pollutants, trace contaminants and toxicity. Before the Regulations for municipal STPs are promulgated, background data on STP effluent toxicity are required to establish toxicity limits using accepted toxicity testing protocols. This paper discusses the study methodology used to generate the database which will support development of the toxicity testing requirements in MISA Municipal Sector Regulations.

### 1.2 Background

In 1987, a literature review commissioned by MOE examined municipal STP effluent toxicity, with particular emphasis on Ontario effluents. The review determined that:

- Primary effluents are generally acutely lethal;
- Secondary and lagoon effluents exhibit varying toxicity, suggesting site-specific factors are involved;
- STP process operating efficiency, as measured by ammonia-N concentration, appears a more reliable determinant of effluent lethality than type or amount of industrial input; however the data on industrial inputs were limited;
- Chlorine and ammonia were the most readily identified toxicants in municipal effluents;
- Information on sublethal or chronic toxicity of municipal STP effluents was very limited.

The literature review identified that key information was lacking, particularly with regards to industrial contribution to municipal effluent toxicity, and the sublethal and chronic toxicity of these discharges. Consequently, a survey to sample and test Ontario STP effluent toxicity was considered necessary prior to Regulation development.

## 2.0 OBJECTIVES

The overall objective of the study was to develop a municipal effluent database which would identify and quantify the constituents and process operating parameters which influence acute and chronic/sublethal effluent toxicity.

Specific objectives in the study were to:

1) Assess the relative contribution of total residual chlorine (TRC), ammonia ($NH_3$) and non-conventional "residual" pollutants to the acute and chronic toxicity of STP effluents.

2) Determine whether or not non-conventional pollutants from indirect industrial discharges significantly contribute to the acute and/or chronic effluent toxicity.

3) Determine the acute and chronic toxicity removal efficiency of nitrifying treatment systems when they operate at maximum (Summer) and minimum (Winter) levels of performance.

4) Attempt to confirm the acute toxicity threshold concentration for unionized ammonia in the STP effluent as the historical data reviewed in the initial literature study were too limited.

5) Compare the acute toxicity of grab samples and 24 hour composite samples of municipal STP effluent.

## 3.0 PROJECT DESCRIPTION

Final treated effluent is sampled for toxicity testing over four weekdays at ten Ontario sewage treatment plants during two seasonal periods. Eight of the STPS have secondary treatment while the remaining two STPs have lagoon treatment systems which discharge on a continuous basis over the year. Plants with primary treatment only were not included in this project, based on the literature review.

At each STP, in both Winter and Summer, each 24 hour composite effluent sample is evaluated for acute and chronic toxicity and specified physical/chemical constituents. Grab samples are collected at a few specific STPs to identify temporal variations in effluent toxicity. Only acute toxicity is tested in the grab samples. Acute toxicity is measured by a 48 hour *Daphnia magna* test and a 96 hour rainbow trout lethality test. Chronic tests include a 7-day fathead minnow survival/growth test and a 7-day *Ceriodaphnia dubia* survival/reproduction inhibition test.

A limited effluent chemistry testing program is conducted to assess the performance of the STP and general characteristics of the final effluent. Physical and chemical parameters measured include free and total chlorine, conventional pollutants including nitrate and nitrite, selected metals, and, in the case of lagoon samples, hydrogen sulphide. TRC, free chlorine, ammonia and pH are determined on-site when the sample is collected and at the toxicity testing laboratory when the tests begin. At the conclusion of the rainbow trout and fathead minnow tests, pH, ammonia and nitrite are measured again to assess any change during the tests.

For effluent samples where non-conventional pollutants are suspected to be contributing significantly to an observed acute or chronic toxicity response (i.e. samples in which there is still residual toxicity following TRC and unionized ammonia reduction steps), specific organic chemical analyses may be undertaken.

A number of procedures were implemented to ensure sample integrity. These included:

- Sample collection using glass, stainless steel, teflon or food-grade polyethylene components;
- Sample collected to minimize headspace and loss of volatile components from composite samples;
- Temperatures control between 5 to 15°C during sample collection, shipment and storage;
- Delivery of effluent samples to the toxicity testing laboratory within sixteen hours of sample collection, and initiation of rainbow trout and *Daphnia magna* tests within 24 hours of sample collection.

In order to ensure that the toxicity data collected at these STPs are representative of "typical" plant operation, operational records and performance data for the week prior to toxicity sampling as well as the week of toxicity sampling are reviewed. In secondary plants, this review includes measurements of process efficiency (removal of $BOD_5$ TSS, TP) and SRT or F:M. In plants which do not routinely monitor raw sewage, primary effluent (if appropriate) and final effluent, these streams are analyzed at least twice per week in the week preceding sample collection for toxicity testing. This characterization includes $BOD_5$, TSS, TP TKN, $NH_3$, $NO_2$, $NO_3$ and pH so that process performance can be defined.

## 4.0 TOXICITY TESTING TRIGGERS

An important component of the toxicity testing program is the identification of toxicants other than well-documented ones such as chlorine and unionized ammonia. To this end, triggering mechanisms have been included in the testing procedures that will eliminate chlorine as a factor in both acute and sublethal tests, and ammonia in the sublethal tests only. Chlorine is removed in one of two parallel test series by reduction with sodium sulphite if the TRC concentration is greater than 0.10 mg/L when the toxicity tests are initiated. This allows assessment of chlorine as a toxicant and enables assessment of other potential sources of toxicity. If the calculated concentration of unionized ammonia is greater than 0.1 mg/L, the effluent to be used for the chronic tests (either as received or dechlorinated if appropriate) is treated with sulphuric acid to a pH of 6.0±0.1 to suppress the unionized ammonia level. This procedure is used to determine whether residual toxicity remains after both chlorine and ammonia are eliminated as toxicants.

Reduction of pH to suppress unionized ammonia can result in changes to effluent quality and, hence, is not without complications. It is known, for example, that several metal species become more soluble, and, thus, may be more toxic, as pH declines from neutrality. This procedure, however, was deemed to cause the least disruption to the original effluent characteristics when compared to ammonia removal by: a) pH elevation followed by air stripping and neutralization; or b) Treatment by clinoptilolite resin. The testing protocol for composite samples is outlined in Figure 1.

The decision to analyze samples for trace organic compounds is based on chronic and sublethal test results. A sublethal EC50 concentration of 30% or lower is usually enough to trigger the analysis for trace organics, although this is tempered by judgement and cost factors. Total and filtered metal analyses are routinely performed on all effluent samples prior to the toxicity tests.

## 5.0 SITE SELECTION

The intent of the study is to evaluate toxicity of effluents discharged by those STPs which typify efficient plant operation. Two principal criteria imposed as a result of this intent were hydraulic capacity utilized, and $BOD_5$ removal efficiency. The specific criteria imposed were that the annual average daily flow must range between 70 - 90% of design hydraulic capacity, and $BOD_5$ removal efficiency must be greater than 80% on an annual average basis.

Evaluation of ammonia as a toxicant is also critical, and so plants have been selected that display seasonal ammonia removal. Finally, plants have been selected that represent a cross-section of industrial inputs, based on discussion with MOE and municipal officials and on the literature review preceding the field sampling.

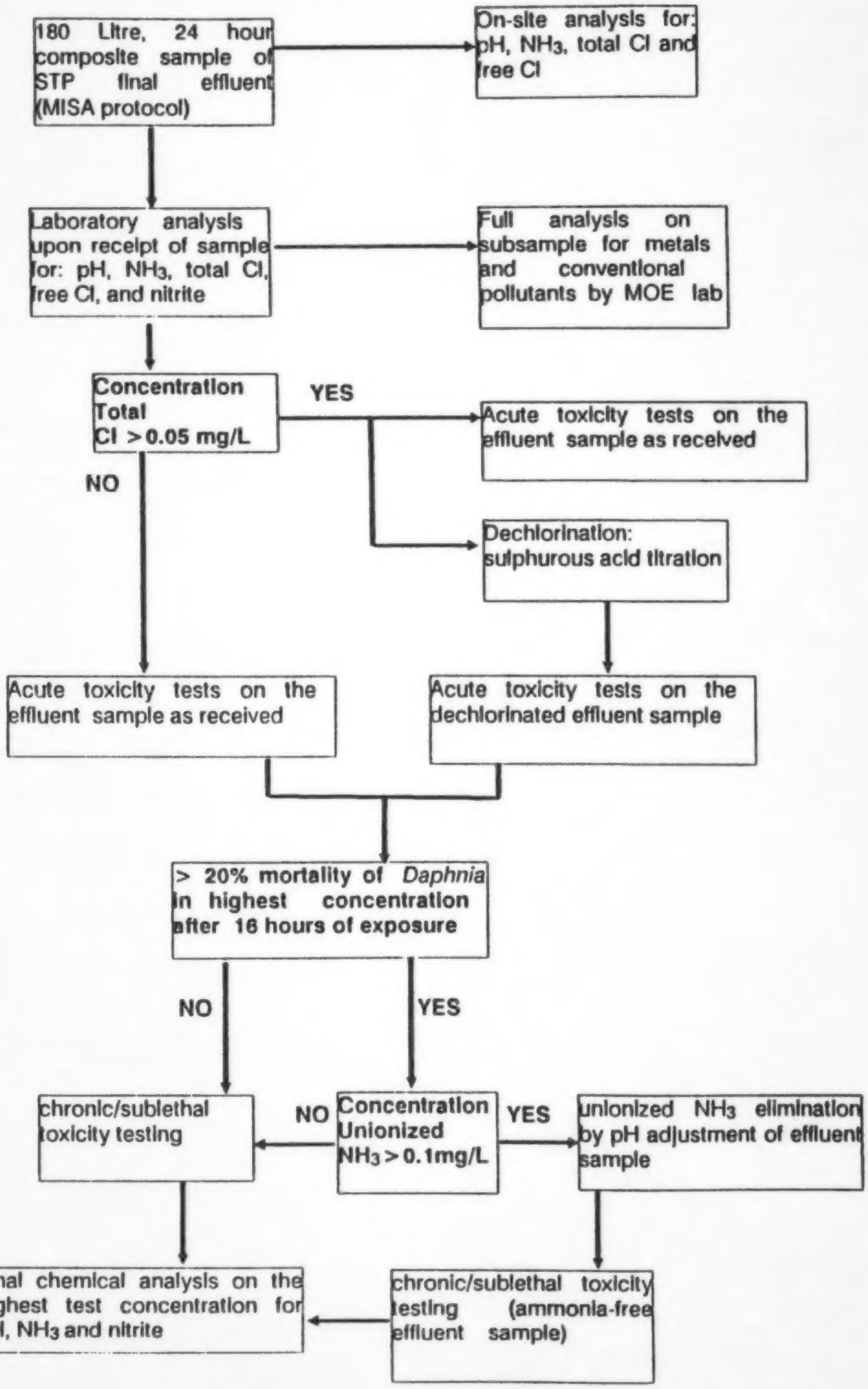
## 6.0 STATUS OF PROJECT

Three sewage treatment facilities (2 secondary plants and one lagoon) were sampled in March 1989 as part of the Winter Program. All ten facilities have been tested in the Summer program from June to September of 1989.

Acute lethality, measured as LC50 (concentration causing 50% mortality of test organisms), has ranged from 10% to greater than 100%. Sublethal toxicity measured as EC50 (concentration causing reduced growth or brood size in 50% of test organisms) has ranged from 1% to greater than 100%. Chlorine appears to be a frequent toxicant, while ammonia has been found to be toxic in few cases. This may be expected during the warm weather season. Metals have not yet been identified as causing acute lethality.

The Winter program will commence again in December 1989 to January 1990, and continue through to March 1990.

FIGURE 1: EFFLUENT CHARACTERIZATION AND TOXICITY TESTING PROGRAM - OVERVIEW AND DECISION POINTS FOR COMPOSITE SAMPLES


180 Litre, 24 hour composite sample of STP final effluent (MISA protocol)
On-site analysis for: pH, $NH_3$, total Cl and free Cl
Laboratory analysis upon receipt of sample for: pH, $NH_3$, total Cl, free Cl, and nitrite
Full analysis on subsample for metals and conventional pollutants by MOE lab
Concentration Total Cl > 0.05 mg/L
YES
NO
Acute toxicity tests on the effluent sample as received
Dechlorination: sulphurous acid titration
Acute toxicity tests on the effluent sample as received
Acute toxicity tests on the dechlorinated effluent sample
> 20% mortality of Daphnia in highest concentration after 16 hours of exposure
NO
YES
chronic/sublethal toxicity testing
NO
Concentration Unionized $NH_3$ > 0.1mg/L
YES
unionized $NH_3$ elimination by pH adjustment of effluent sample
Final chemical analysis on the highest test concentration for pH, $NH_3$ and nitrite
chronic/sublethal toxicity testing (ammonia-free effluent sample)

Acute toxicity tests: *Daphnia magna* 48 hour acute lethality test
*Salmo gairdneri* 96 hour acute lethality test
Chronic/sublethal tests: *Ceriodaphnia dubia* 7 day reproduction and survival test
*Pimephales promelas* 7 day larval growth and survival test
( 8 dilutions for each chronic bioassay )

# ENVIRONMENTAL PATHWAYS OF CONTAMINANTS IN WATERS RECEIVING MUNICIPAL/INDUSTRIAL EFFLUENTS

Dr. John Carey,
Environment Canada,
National Water Research
Institute

## ABSTRACT

The presentation summarized studies of the transport, fate and effects of organic compounds in waters receiving effluents from sewage plants. The types of organics observed fall into three groups:

(i) Compounds directly related to sewage, eg., fatty acids, caffeine, nicotine;
(ii) Synthetic organic compounds present in the influent to the sewage plant and discharged unchanged, eg. PCBs, pentachlorophenol, dichlorobenzene; and
(iii) Transformation products of compounds present in the plant influent eg. surfactant and drug degradation products.

Many compounds are discharged adsorbed on solids and desorb slowly. Such compounds are useful as tracers to define the extent of transport and impact of sewage plant discharges. Examples of these compounds include coprostanol, tocopherol acetate and alkylbenzene sulfonates.

The fate of sewage related contaminants is governed by the rates of various transformation pathways including photolysis, hydrolysis and biodegradation. These processes are best studied in the laboratory and extrapolated to the field. Specific examples were presented.

Although impacts of sewage plant effluents in receiving waters can be studied using benthic community assessments and indicator species, field studies of effects are hampered by the inability to differentiate between effects of the contaminant and those due to effects of the effluent itself,eg. changes in dissolved oxygen.